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Field experiments designed to evaluate deoxygenation of natural seawater as a corrosion control measure for unprotected seawater ballast tanks demonstrated decreased corrosion in hypoxic (<0.2 ppm O_2) seawater using weight loss and linear polarization measurements. The experiments also demonstrated the difficulty of maintaining hypoxic seawater. Using a gas mixture it was possible to displace dissolved oxygen in natural seawater. However, aerobic respiration and corrosion reactions consumed oxygen and produced totally anaerobic conditions within the first days of hypoxia. When gaskets and seals failed oxygen was inadvertently introduced. The impact on corrosion depended on the amount of dissolved oxygen in the system at the time of the inadvertent oxygen introduction. Steels exposed to cycles of hypoxic seawater and oxygenated atmosphere had the highest corrosion rate and severity.

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CORROSION 2005

EVALUATION OF DEOXYGENATION AS A CORROSION CONTROL MEASURE FOR BALLAST TANKS

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ABSTRACT

Field experiments designed to evaluate deoxygenation of natural seawater as a corrosion control measure for unprotected seawater ballast tanks demonstrated decreased corrosion in hypoxic (< 0.2 ppm O_2) seawater using weight loss and linear polarization measurements. The experiments also demonstrated the difficulty of maintaining hypoxic seawater. Using a gas mixture it was possible to displace dissolved oxygen in natural seawater. However, aerobic respiration and corrosion reactions consumed oxygen and produced totally anaerobic conditions within the first days of hypoxia. When gaskets and seals failed oxygen was inadvertently introduced. The impact on corrosion depended on the amount of dissolved oxygen in the system at the time of the inadvertent oxygen introduction. Steels exposed to cycles of hypoxic seawater and oxygenated atmosphere had the highest corrosion rate and severity.

INTRODUCTION

Deoxygenation of seawater has been demonstrated as an environmentally friendly ballast water treatment to control introduction of non-native aquatic species.[1] Investigators have proposed that the same treatment provides a low-cost, effective corrosion control measure for uncoated carbon steel ballast tanks based on the concept that reducing oxygen from the ballast tanks will limit oxidation.[1, 2] Matsuda *et al.*[2] conducted shipboard trials by sealing a ballast tank at the deck and installing vertical pipes into the headspace. They reported that pumping pure nitrogen gas into the headspace for 1.5 hr reduced oxygen levels in the seawater to approximately 0.2 mg/L and decreased the rate of uniform corrosion of carbon steel by 90%, as determined by weight loss. Matsuda *et al.*[2] did not include the normal ballast tank operational practice of cycling between filled and emptied tanks nor did they investigate the consequences of introducing additional oxygen. Furthermore, there was no evaluation of localized corrosion.

Previous laboratory experiments[3, 4] comparing corrosion resulting from stagnant aerobic natural seawater with corrosion resulting from stagnant anaerobic natural seawater over a one-year period demonstrated the following: (1) corrosion was more aggressive under totally anaerobic conditions as measured by instantaneous corrosion rates ($1/R_p$) and weight loss, (2) under aerobic conditions corrosion was uniform and the surface was covered with iron oxides (lepidocrocite and goethite) and (3) under anaerobic conditions the corrosion was localized pitting and the corrosion products were mackinawite and pyrrothite.

Several investigators[5-7] have suggested that the most corrosive operating condition is one in which carbon steel is exposed to alternating oxygenated/deoxygenated seawater. Under constant oxygenation an oxide will form that provides corrosion resistance. Under anaerobic conditions, sulfate-reducing bacteria (SRB) produce sulfides, resulting in conversion of the oxide to a sulfide. The result of repeated oxygenated/deoxygenated cycles is reportedly severe localized corrosion, i.e., pitting. Most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium.[8] Anaerobic conditions and sulfides can form within marine biofilms at biofilm/metal interfaces, independent of bulk oxygen concentrations.[9]

Field experiments were designed to evaluate deoxygenation as a corrosion control measure for uncoated carbon steel ballast tanks exposed to natural seawater when tanks were maintained with cycles of potential operating conditions: (1) oxygenated seawater followed by an oxygenated atmosphere, (2) deoxygenated seawater followed with an oxygenated atmosphere and (3) deoxygenated seawater followed with a inert atmosphere (majority nitrogen, carbon dioxide, trace oxygen). Results are compared with the previously reported results for carbon steel exposed in the laboratory to stagnant aerobic and totally anaerobic natural seawater.[3, 4] The field experiments described in this paper were not designed to produce totally anaerobic conditions, but were meant to approximate the level of oxygen described in the Matsuda experiments[2] i.e., 0.2 ppm.

MATERIALS AND METHODS

Three identical chambers were built to expose 1020 carbon steel (common ballast tank material) and natural seawater to different conditions (Figure 1). The chemical composition of 1020 carbon steel is listed in Table 1. Chambers were cylindrical (35.5 cm diameter and 27.9 cm height) made from heavy gage, chemical resistant, opaque polyethylene. Corrosion coupons were 1020 carbon steel (Table 1), 1.5 cm dia. x 0.16 cm thick (Metals Samples®, Munford, AL) with as-mill finish. Individual insulated wires were attached to the back of each sample and held in place using conductive silver adhesive (Electron Microscopy Sciences®, Fort Washington, PA) and carbon tape. The exposure side of the coupon was coated with vacuum grease and centered face down inside a plastic mount (3.175 cm dia. x 2.5 cm height). Samples were mounted in Epothin® epoxy (Buehler®, Lake Bluff, IL) with the wire connection exposed and allowed to cure for 24 hrs. Vacuum grease prevented epoxy from getting between the sample face and the bottom of the mount and allowed the as-mill finish to be preserved. Epoxy-mounted carbon steel coupons were orientated in rows both horizontally (27 samples) and vertically (9 samples) in each chamber to simulate tank bottoms and sidewalls, respectively, for a total of 36 samples (Figure 2). A heavy gauge plastic cylinder (17 cm dia. x 23 cm height) held the electrodes in place with the vertically oriented samples positioned inwards and the horizontally oriented samples positioned upwards. Prior to seawater exposure, coupons were rinsed in acetone, ethanol and distilled water and

dried with nitrogen gas to removed vacuum grease and residual surface debris. As shown in Figure 1, a Ag/AgCl electrode and a platinum/niobium mesh were used as reference and counter electrodes, respectively. The counter electrode mesh was 225 cm^2 in area (15 cm x 15 cm) with a cylindrical shape to maximize current distribution to all sample electrodes.

Each of the three chambers was maintained with a defined operating condition (Table 2). (As a side note, Tanks 2 and 4 were used in a separate experiment from the one reported here). In all cases the natural seawater was from Key West, FL. Chambers were cycled between 2-week seawater exposures and 2 weeks of atmospheric exposures. The chambers varied as to whether the seawater had been deoxygenated and whether the atmospheric gas was air or an inert gas mixture. All chambers were maintained at NRL Corrosion Laboratory, Key West, FL. Cycles were repeated for one year. Coupons in Tank 1 were exposed to cycles of alternating between natural oxygenated seawater and air. Coupons in Tank 3 were exposed to alternating deoxygenated natural seawater and air. Coupons in Tank 5 were exposed to alternating deoxygenated natural seawater and inert gas containing only trace amounts of oxygen. Natural seawater was deoxygenated using an inert gas as water was pumped into the tanks. The inert gas was premixed and stored in a gas cylinder. The gas was mixed with ballast water using an in-line injector downstream of the ballast pump. The system is designed so that the inert gas was also used to blanket all headspaces and the entire chamber when empty to maintain continuous hypoxia. After draining, from a side valve located near the bottom of the tank, a small layer (2.5 cm deep) of seawater remained in the bottom of all tanks so that bottom row electrodes (Row 4) had a thin (~ 1mm) layer covering them and were wet throughout the experiment.

Natural seawater before and after deoxygenation was examined for dissolved and particulate water chemistry. The following parameters were measured: dissolved oxygen, salinity, temperature, bulk pH, and sulfide. Sulfide concentrations were determined in triplicate by extracting 1 ml, diluting to 1:10 with double distilled water, and employing the methylene blue method 228 C (Standard Methods 1971). A Hach® Odyssey DR2500 spectrophotometer and the manufacturer's built-in program were employed in this technique. A sterile 5 ml syringe was used to remove 4 ml from the 20 ml water sample. One ml was used to inoculate serial dilutions (10^5) of each the following seawater media (Dixie Testing and Products, Inc.®, Houston, TX): phenol red dextrose broth (Difco®), Postgate medium B, nutrient broth (Difco®) and thioglycollate medium (Difco®) used to determine most probable numbers of acid-producing bacteria (APB), sulfate-reducing bacteria (SRB) and general heterotrophic aerobes and anaerobes, respectively. Dilutions were incubated for 28 days at room temperature.

Four coupons (1 horizontally and 3 vertically orientated) were removed every 1 – 3 months. Coupons were fixed in 4% glutaraldehyde in filtered seawater and rinsed in distilled water. Environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) were used to characterize the corrosion morphology, biofilm structure and corrosion product composition on the metal surface. X-ray diffraction (XRD) was used to determine the mineralogy of the corrosion products on 3-4 coupons throughout the year-long exposure. Open-circuit potential was monitored continuously using a Agilent® HP34970A data logger and linear polarization resistance (LPR) was performed on each sample every 1-3 months using a Gamry® PC4-300 potentiostat with IR correction enabled. Dissolved oxygen (DO) in each container was monitored continuously using a dissolved oxygen electrode (OxyGuard® DO Probe, Port Moody, British Columbia, Canada) and mini data logger (MadgeTech® Model Volt101-100mV, Warner, NH). The DO probe was immersed in the midsection of the chamber so that during a fill cycle the probe was at a height between electrode Rows 2 and 3, with the water level being just above Row 1 (Figure 2). During drain cycles, the probe recorded atmospheric oxygen concentration.

RESULTS

At the onset of the experiment in April 2003, natural Key West seawater (before and after deoxygenation) physical chemistry and bacterial populations were examined and have been reported in Tables 3 and 4, respectively. Raw seawater had a pH of 8.02 while the deoxygenated seawater had a pH of 6.23. The drop in pH was due to CO_2 in the process gas mixture dissolving into the water. Sulfide concentration was negligible in the parts-per-billion range. Deoxygenation resulted in the removal of DO from the raw seawater level of 6.5 parts-per-million (ppm) to less than 0.1 ppm. Deoxygenation also had an affect on the culturable bacterial counts of the seawater. As shown in Table 4, raw seawater had high concentrations of aerobes, general anaerobes and APB, but no culturable SRB. Water and bacterial samples from Tanks 1, 3, and 5 were also examined after a 14 day wet cycle during the exposure period of 74 – 98 days (Table 5). The pH fluctuated within narrow ranges. The pH in Tank 5 increased from the initial value of 6.23 to 6.57, and in Tank 1, dropped from the initial value of 8.02 to 7.42. Sulfide concentrations in all tanks increased by an order of magnitude from initial conditions (Tables 3 & 5). Culturable SRB counts increased in Tanks 1 and 3 to 10^5 and 10^6, respectively, while no culturable SRB were measured in Tank 3.

DO measurements were made throughout the experiment during both the fill and empty cycles (Figure 3a). The DO concentration in the deoxygenated water was consistently higher than the design value of 0.2 mg/L for Tank 5. Similarly, the atmosphere in Tank 5 contained oxygen levels that were similar to Tanks 1 and 3. Reasons will be presented in the discussion section. In all three chambers, the oxygen level was highest during the exposure to atmospheric conditions (Figure 3a). Electrochemical measurements were made during fill and empty cycles. During early portions of the experiment (days 0-100 days) draining the water had a profound influence on E_{corr} measurements in all chambers as represented by gray shaded regions in Figures 4 – 8. This phenomenon was due to an open (incomplete) circuit between the carbon steel coupons and the reference electrode in the absence of the seawater electrolyte. However, at times after 100 days exposure, as a NaCl containing layer was deposited throughout the chamber, E_{corr} values were stable even after draining. The salt film and the high humidity within the chambers formed a salt bridge between the working and reference electrodes. E_{corr} values of Rows 1 – 3 had the greatest difference between fill and empty cycles. The impact of draining was less for the bottom samples (Figure 8c) than for coupons on the sides of the tanks (Figures 7b,c & 8b). E_{corr} values for the bottom samples tended to be consistently low and unaffected by the fill/drain cycle for all three chambers (Figure 8c). This trend is particularly evident in E_{corr} data for Tank 5 (Figure 6) when compared to data from Tank 1 (Figure 4) and Tank 3 (Figure 5). E_{corr} data for bottom samples of Tank 5 were stable, while the data for the sides were erratic, even at longer times.

In general all exposure conditions produced a two-tired corrosion layer. The outer extremely fragile layer was reddish orange and XRD data indicated halite, lepidocrocite and goethite. The inner layer was black, tenacious and XRD indicated maghemite. The specific appearance of the electrodes varied with oxygen concentration in the water or atmosphere at the time of collection (Figure 9). Images in Figure 9 represent a single row of electrodes (Row 2) collected at 98, 146, 237 and 395 days. At 98 days the outermost corrosion layer was predominately black with some reddish-orange superficial deposits. The coupon was collected after exposure to seawater with less than 1 ppm DO. The coupon

collected at 146 days had been exposed to 40 days of an atmosphere containing 6 ppm DO and the surface was covered with a reddish-orange corrosion layer. The coupon, collected at 237 days after exposure for 2 weeks to seawater containing approximately 0.2 ppm DO, was covered in a black layer. The sample collected at 395 days had been exposed to seawater containing 1 ppm DO and had a reddish-orange appearance. Images in Figure 10 represent differences in appearance between side and bottom electrodes. Figure 10a indicates an electrode from Tank 3 Row 1 at the conclusion of the experiment (395 days exposure). The electrode surface is black or dark grey with small patches of reddish orange. Figure 10b an electrode after the same exposure period (395 days) from Row 4. The appearance of electrodes exposed on the bottom is very different from that of Row 1 having an outer layer of reddish orange which covers the entire surface. Close inspection shows dark regions below the outer surface. All outer layers contained concentrations of twisted bacterial filaments that, in some cases, were encrusted in iron (Figure 11). EDS spectra identified the presence of sulfur in the corrosion products formed on samples in Tank 5 after 299 days total exposure and a hypoxic condition for 10 days. All other samples had only minor amounts of sulfur associated with the corrosion products. The appearance of the electrodes gave no indications of the type, severity or distribution of the corrosion (Figure 12). Figures 12a and 12c were taken from the sides and bottom of Tank 1, respectively. They have a similar two-tiered corrosion layer. Coupons removed from the side (Figure 12b) were pitting over roughly one-half of the surface. Coupons exposed on the bottom were uniformly covered with general corrosion (Figure 12d).

Instantaneous corrosion rates ($1/R_p$ reported in units of $ohms^{-1}$) were measured using the LPR technique every 30 – 60 days on all electrodes in each chamber and are reported as average values in Figures 13 and 14 sorted by tank and row, respectively. Corrosion rates were not normalized by electrode area since all electrodes were equivalent in size. $1/R_p$ data for Tank 1 (Figure 13a) indicates side Rows 1, 2 and 3 corroded at rates 1.5 – 3 times faster than the bottom Row 4 over the first 170 days. After 170 days, the corrosion rates of the sides dropped below that of the bottom and remained lower until 395 days when all rows were corroding at the same rate. The corrosion rates of the sides were very dynamic in comparison to the rate for the bottom, which was relatively flat. The side rows showed the largest range (0.0015 – 0.013 $ohms^{-1}$) of rates over the experimental period time, while those of the bottom row) had a much smaller range of (0.0015 – 0.006 $ohms^{-1}$). $1/R_p$ data for Tank 3 (Figure 13b) indicates that initially, the side Rows 1, 2, and 3 corroded faster than the bottom Row 4. However, at 98 days the bottom row began to corrode slightly faster than the side rows. At 137 days, the corrosion rate for the side rows jumped to 0.022 $ohms^{-1}$ while the bottom row was around 0.005 $ohms^{-1}$. This jump in corrosion rates for vertically oriented side coupons corresponded to measurements taken immediately after a long period (~47 days) of empty cycle exposure with a 7 ppm oxygen concentration in the atmosphere (Figure 3a). It should be noted that the side corrosion rates during this period were twice as high as the largest corrosion rate measured for any rows in Tank 1 for the entire exposure. For the remainder of the experiment, the bottom row corroded at twice the rate of the side rows. At 395 days, bottom row corrosion rate increased to the high rate (0.022 $ohms^{-1}$), which was observed at 137 days for the side rows. $1/R_p$ data for Tank 5 (Figure13c) followed the same trends for first 170 days as that of Tank 3, including a jump in corrosion rates for vertically oriented side samples at 137 days, but to a lower value of 0.012 $ohms^{-1}$. At 170 days, all rows had the same low corrosion rate of 0.001 $ohms^{-1}$. However, at 207 days, the corrosion rates of all rows increased to between 0.007 – 0.01 $ohms^{-1}$ with Row 1 having the highest and Row 4 (bottom) having the lowest rate. This rate increased corresponding again to the measurement taken after another long period empty cycle (46 days) exposure to high atmospheric oxygen levels of 5 ppm. Interestingly, Tanks 1 and 3 were exposed to higher

concentrations of atmospheric oxygen 7 ppm over the same exposure period but did not exhibit the same increase in corrosion rates as vertically oriented electrodes as in Tank 5. After 207 days, corrosion rates of the side rows remained low at 0.001 $ohms^{-1}$ while the bottom row corroded at twice the rate but was still low in comparison to Tank 3. Figure 14 plots the same corrosion rate data as in Figure 13 but sorted by row. Side Rows 1, 2, and 3 all have the same corrosion behavior for a given tank. Tank 3 corrosion rates were the highest while for Rows 1, 2 and 3. Tank 1 side rows seem unaffected by long periods of exposure to high atmospheric oxygen concentrations whereas, side rows of Tanks 3 and 5 are strongly affected in the first 150 days, after which, only Tank 5 is consistently affected by high atmospheric oxygen levels. $1/R_p$ values for Row 4 of all tanks were low initially. The instantaneous corrosion rate for Row 4 (bottom) of Tank 1 stayed stable throughout the experiment, as did Tank 5 Row 4 except for a slight increase at 207 days. At the conclusion of the experiment, Row 4 of Tank 3 was corroding at the highest level of any of the rows in any of the tanks. Figure 15 is the combined data of all tanks and rows with the side rows reported as an overall side average value. As can be seen, Tank 3 Row 4 has the highest corrosion rates over the experiment, while the sides of Tank 1 and all of rows of Tank 5 have the lowest.

Weight loss has been plotted as a function of placement in the three tanks. Figure 16 shows the weight change over time for Tanks 1, 3, and 5 for all four rows. The largest weight loss was measured for Rows 3 and 4 in Tank 1 while in Tank 3, the highest weight change was measured for Rows 1 and 4. No distinction could be made between weight losses of the different rows in Tank 5. The identical data is plotted in Figure 17 plots for all tanks and is grouped by row. Figure 17a includes data for Rows 1 and 2, Figure 17b for Rows 3 and 4. The first two rows in all tanks experienced essentially the same weight loss over time, approximately 0.2 g over 350 days, independent of exposure conditions. Data in Figure 17b are more scattered at later times for Rows 3 and 4 for each tank, with Tank 5 rows having the lowest weight lost. Row 3 lost more in all cases than Rows 1 and 2 and the greatest total weight loss for all three exposures was measured in the horizontally oriented samples on the bottom Row 4.

Data for three periods of frequent data collection are presented in Figures 18-23. All three tanks were filled with seawater (Tank 1 – raw, Tanks 3 and 5 – deoxygenated) on day 136 after an empty cycle. Electrochemical data collection began on day 136 and continued daily until day 146. Figure 18 includes E_{corr}, $1/R_p$ and dissolved oxygen data for Tank 1 for this period. The data indicate that the coupons on the sides are corroding at a rate about 2 times that of the bottom. E_{corr} values for the three rows of side samples are almost identical while that of the bottom sample is much lower. The same general observations were made in Tank 3, however the oxygen was higher, the E_{corr} values were lower and the corrosion rate was higher. Corrosion in Tank 5 showed the same pattern with the side coupons corroding faster than the bottom. E_{corr} in Tank 5 did not increase with an increase in oxygen. The next period of intense data collection covered the period from days 232 to 238 and is shown in Figure 19. Electrochemical data collection started on day 234 (2.3 days after filling). During the interim from day 146 to 231 several changes occurred in the trends of the data. In all cases the coupons on the bottom of the tank were corroding faster than those on the sides. The corrosion rate was highest for the bottom sample exposed in Tank 3. Instantaneous corrosion rates in Tank 5 were 0.002 $ohms^{-1}$ or lower while those for the sides in Tank 3 were around 0.002 $ohms^{-1}$, but the instantaneous corrosion rate for the bottom row was 0.007 $ohms^{-1}$ and that for Tank 1 was 0.004 $ohms^{-1}$. Intense data collection also took place between day 318 and 321, with electrochemical data acquired at the onset of the fill cycle. Figure 20 indicates corrosion rates in Tank 1 ranging from 0.002 to 0.006 $ohms^{-1}$ with the highest rate in the bottom sample. Corrosion rates in Tank 3 were the highest for any of the exposures ranging from 0.007

to 0.013 ohms^{-1} with the highest rates in the bottom row. The lowest corrosion rates were measured in Tank 5 from 0.001 to 0.002 ohms^{-1} with the bottom sample having the highest rate. The identical data was also plot by grouping into rows as shown in Figures 21 – 23. As shown in Figure 21, an interesting observation from the 136 – 146 day exposure period can be seen. Initially, in Rows 1, 2 and 3, Tank 1 coupons are corroding the least but at 140 days Tank 5 coupons drop to the same level. From 140 – 146 days, Tank 5 coupons have the lowest corrosion rates. This trend is not observed in Row 4 where Tank 5 coupons continually had the lowest corrosion rate. For all rows, Tank 3 had the highest corrosion rate. Figure 22 demonstrates that during the 232 – 238 day exposure range, the high corrosion rates were observed in the bottom Row 4 samples; with Tank 3 being the highest and Tank 5 being the lowest. For the final exposure range of 318 – 321 days, Figure 23 shows that for all rows, Tank 3 has the highest corrosion rates and Tank 5 the lowest. Data for highest and lowest corrosion rate by tank, row and overall for each of the three sampling periods are summarized in Tables 6, 7 and 8, respectively.

DISCUSSION

Matsuda *et al.*[2] produced hypoxic natural seawater by bubbling nitrogen gas into the headspace of a partially filled, sealed ballast tank for 1.5 hours. They placed an oxygen sensor in the headspace and deduced that the purge gas equilibrated with the dissolved gases in the water column to produce a DO concentration of approximately 0.2 ppm. They indicated that controlling the oxygen concentration in their shipboard experiments was the most difficult aspect of their experiment. Their DO data (Figure 24), and the field experiment reported in this paper (Figure 3a&b) demonstrate this difficulty. In the initial stages (Figure 3b) of the experiment, it was extremely easy to reduce the oxygen concentration in the bulk seawater to below 1 ppm in Tanks 3 and 5. However, aerobic respiration and abiotic corrosion reactions consumed oxygen readily and drive the DO concentration to zero within days in all tanks. Maintaining a specific hypoxic DO concentration in a sealed tank will require an accurate prediction of probable oxygen consumption, monitoring, and the ability to add oxygen should respiration and corrosion reactions reduce DO below the target concentration. The concentration of DO in the seawater in Tanks 3 and 5 was a direct function of the performance of the gaskets and seals. When the seals held it was possible to maintain decreased oxygen levels in the water. When the seals failed, oxygen diffused into the tanks. While we were unable to maintain the desired hypoxic conditions in the seawater for Tanks 3 and 5 and the atmosphere for empty Tank 5, we can assess the corrosion of carbon steel resulting from the introduction of oxygen into hypoxic water or atmosphere. As seen in Figure 12, peaks in the instantaneous corrosion rates at 137 and 207 days immediately follow prolonged periods of exposure to atmospheric oxygen (Figure 3). Steels that were previously exposed to hypoxic seawater conditions (Tanks 3 and 5) experience a spike in instantaneous corrosion at 137 days. However, only electrodes in Tank 5 had an increase in corrosion rate at 207 days. Also, only corrosion rates of side row electrodes of Tanks 3 and 5 were affected by prolonged exposures to empty cycles containing an oxygenated atmosphere. Bottom rows were unaffected because of the residual water at the bottom of the tanks which remained after draining which prevented the steel from cycling completely between wet and dry conditions. Bottom row electrodes were never allowed to completely dry. Reduction of DO in the water and atmosphere in Tank 5 produced the desired effect of reducing corrosion as measured by weight loss and linear polarization techniques. However, introduction of oxygen caused an immediate increase in the corrosion rate. These results confirm the earlier experiments of Hardy and Bown[5] and Lee *et al.*[6, 7] However, our data demonstrate an important practical consideration not previously discussed by other authors. The increase in instantaneous corrosion rate does not correspond directly with the amount of oxygen introduced at any one time. Instead the increase is related to the prevailing oxygen concentration at the time oxygen is introduced.

Hamilton[8] recently proposed a model for microbiologically influenced corrosion (MIC) in which he reviewed MIC and concluded that all mechanisms involved a process of electron transfers from base metal to oxygen as the ultimate electron acceptor through a series of coupled reactions. The specific coupled reactions varied with mechanism and causative organism. In the case of SRB, sulfate, an intermediate electron acceptor, is reduced to sulfide which reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. Consistent with that model, most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium.[9, 10] Key West, FL, seawater typically contains 2 g/L sulfate and 5-7 mg/L (ppm) DO. Lee *et al.*[3, 4] recently demonstrated that oxygen was not required for localized corrosion of carbon steel exposed to seawater. In fact, they demonstrated more aggressive, localized corrosion of carbon steel in totally anaerobic stagnant natural seawater than in oxygenated stagnant natural seawater. They further demonstrated that introduction of oxygen to the totally anaerobic chamber caused an immediate increase in weight loss and instantaneous corrosion rate. The $1/R_p$ data from those stagnant experiments are compared with the cycling data in Figure 25. Stagnant aerobic conditions had the lowest corrosion rates while the bottom row of the stagnant anaerobic case had the largest (until the end of the exposure period at which time the side rows had the largest). $1/R_p$ data from all cycling experiments were intermediate between those extremes.

Neither weight loss nor LPR measurements provide an absolute quantification of the types of corrosion we observed in the samples. Weight loss is an average of material lost from the surface and is best suited for approximations of general, not localized corrosion. Weight loss measurements, as in the case of the Matsuda *et al.*[2] measurements, do not provide insights into pitting. Intense localized pitting can produce small weight losses. In the experiments reported in this paper, weight loss and LPR data indicate the same basic trends and both can be used for comparing relative corrosion rates. However, pitting could only be described after acid-cleaning the specimens and examining them directly. Our XRD, ESEM and EDS measurements demonstrate that it is possible to document precisely the mineralogy, microbiology and chemical composition of corrosion layers at specific times, however it is not possible to use those data to predict type of corrosion, severity or distribution. In all cases these data were influenced by the oxygen concentration at the time of sample collection.

Despite the presence of bacteria in all surface corrosion products and measurement of a diverse microbial microflora in the bulk seawater medium, it is impossible to elaborate on the role/mechanisms of MIC in the cycling experiments. Bacterial types were quantified in the seawater at the start of the experiment and after stagnation. It is generally recognized that only a small percentage of the natural microflora can be cultured using selective culture media and a single incubation temperature. Furthermore the organisms cultured from the bulk medium cannot be used to approximate the numbers and types of organisms on the surface. It is interesting to note that SRB could not be cultured from the natural seawater at the time of collection. After 14 days, SRB were cultured from the stagnant waters in Tanks 1 and 5, but not Tank 3. Periods of deoxygenation could increase localized corrosion resulting from the activities of naturally occurring microaerophilic, facultative or obligate anaerobic bacteria. Seawater contains 2 g/L sulfate than can be reduced to sulfide by SRB in the absence of oxygen. Deoxygenation can also result in putrefaction, anaerobic breakdown of sulfur-rich proteins, and levels of sulfides will not be limited to the sulfate concentration in the seawater. Sulfide reacts with iron oxide, formed in the atmosphere or in oxygenated seawater, to produce a non-tenacious iron sulfide layer that can be removed with stress or converted back to an oxide by the introduction of oxygen. In either case the sulfide layer is not uniformly removed or oxidized, creating adjacent anodic and cathodic regions and aggressive corrosion. Again, these "snap-shots" of the microbial population are interesting, but cannot be interpreted as to their impact on the corrosion.

CONCLUSIONS

- Any attempts to use deoxygenation as a corrosion control measure will have to consider both the consumption of oxygen by aerobic respiration and corrosion reactions, as well as the introduction of oxygen from the atmosphere.

- Introduction of oxygen into an anaerobic/hypoxic system resulted in an increase in corrosion rate and severity. Neither can be predicted based on the concentration of introduced oxygen.

ACKNOWLEDGEMENTS

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TABLES

Table 1. Chemical composition of carbon steel 1020.

AISI-SAE designation	C	Mn	P max	S max	Fe
1020	0.17-0.23	0.3-0.6	0.04	0.05	balance

Table 2. Operating conditions of the three experimental chambers*.

Chamber designation	Wet cycle condition / Headspace content	Atmospheric cycle condition
Tank 1	Natural seawater / Air	Air
Tank 3	Deoxygenated seawater / Air	Air
Tank 5	Deoxygenated seawater / Inert gas	Inert gas

* Tanks 2 and 4 were used for laboratory studies and are not included in this paper.

Table 3. Bulk Key West seawater physical chemistry.

Water Condition	pH	Sulfide (ppm)	Dissolved Oxygen (ppm)	Salinity	Temperature (°C)
Raw Seawater	8.02	<0.03	6.5	38	28
Deoxygenated Seawater	6.23	<0.03	<0.1	38	28

Table 4. Most probable number of bacteria for raw seawater at the onset of the experiment.

Water Condition	Aerobes $(10)^X$	Anaerobes $(10)^X$	APB $(10)^X$	SRB $(10)^X$
Raw Seawater	4	3	4	0

Table 5. Physical water chemistry and bacteria counts after 14 day wet cycle for all tanks.

Tank	pH	Sulfide (ppm)	Aerobes $(10)^X$	Anaerobes $(10)^X$	APB $(10)^X$	SRB $(10)^X$
1	7.42	0.12	1	2	2	5
3	7.29	0.18	3	3	3	0
5	6.57	0.20	2	2	2	6

Table 6. Highest and lowest instantaneous row corrosion rates grouped by tank for each of the three time spans.

	Tank	1	1	3	3	5	5
Exposure range (days)	*Rank*	Highest	Lowest	Highest	Lowest	Highest	Lowest
136 – 146	*Row(s)*	2	4	2	4	1	4
232 – 238	*Row(s)*	4	1,2,3	4	1,2,3	4	1,2,3
318 - 321	*Row(s)*	4	3	1,2,3,4	-	4	1,2,3

Table 7. Highest and lowest instantaneous row corrosion rates grouped by row for each of the three time spans.

	Row	1	1	2	2	3	3	4	4
Exposure range (days)	*Rank*	Highest	Lowest	Highest	Lowest	Highest	Lowest	Highest	Lowest
136 – 146	*Tank(s)*	3	1/5*	3	1/5*	3	1/5*	3	5
232 – 238	*Tank(s)*	3	5	3	5	3	5	3	5
318 - 321	*Tank(s)*	3	5	3	5	3	5	3	5

* Initially, Tank 1 had the lowest corrosion rates but at later times, Tank 5 was lower.

Table 8. Highest and lowest instantaneous row corrosion rates overall.

Exposure range (days)	Highest	Lowest
136 – 146	Tank 3 – Row 2	Tank 5 – Row 4
232 – 238	Tank 3 – Row 4	Tank 5 – Rows 1 & 2
318 - 321	Tank 3 – Rows 3 & 4	Tank 5 – Rows 1 & 2

FIGURES

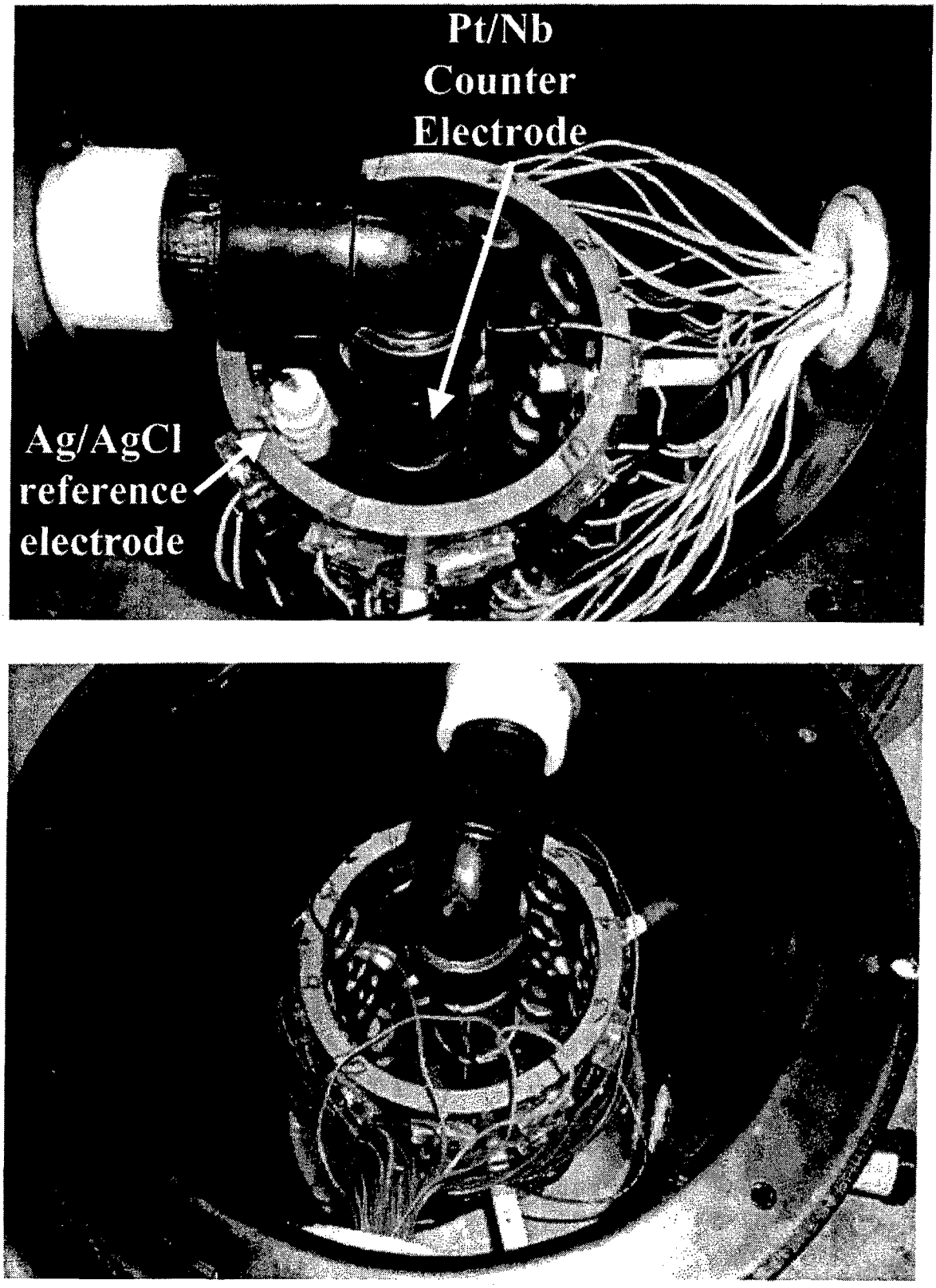
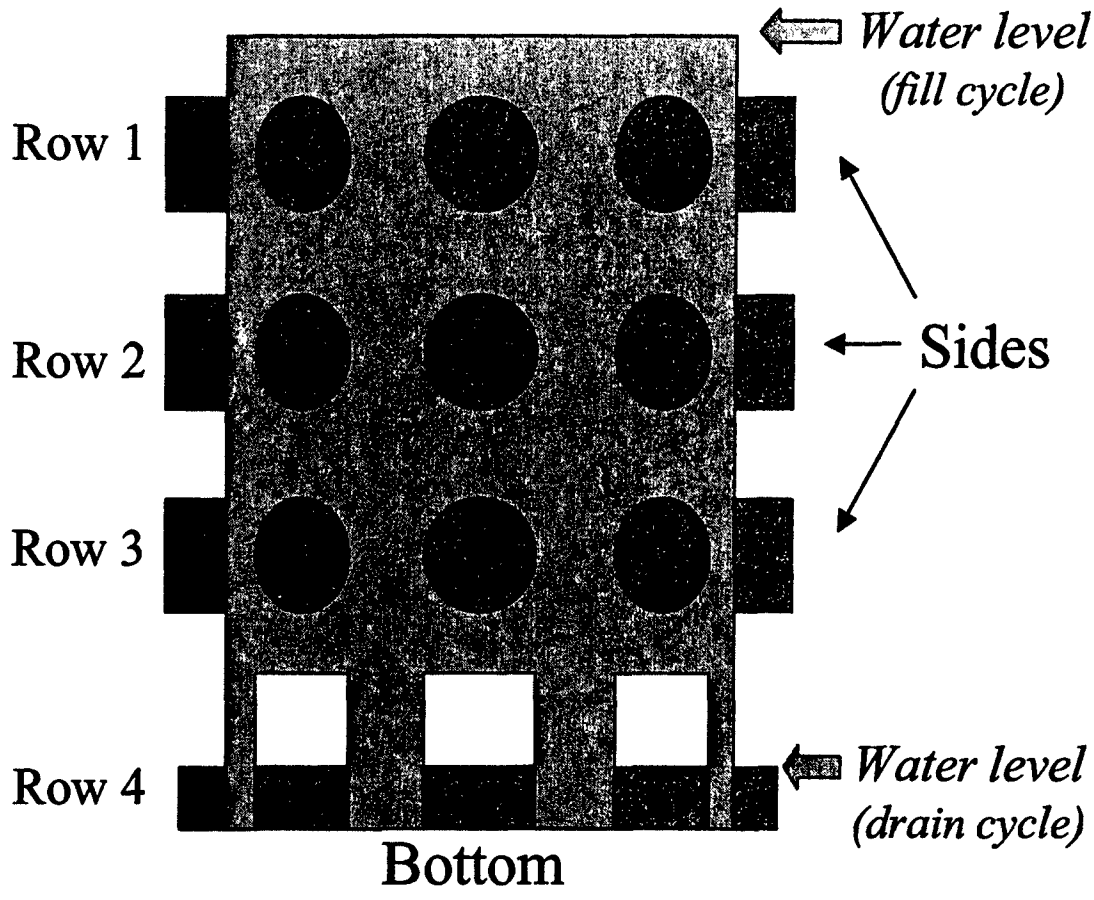


Figure 1. Experimental chamber used to examine rates and mechanism of corrosion under deoxygenated conditions.



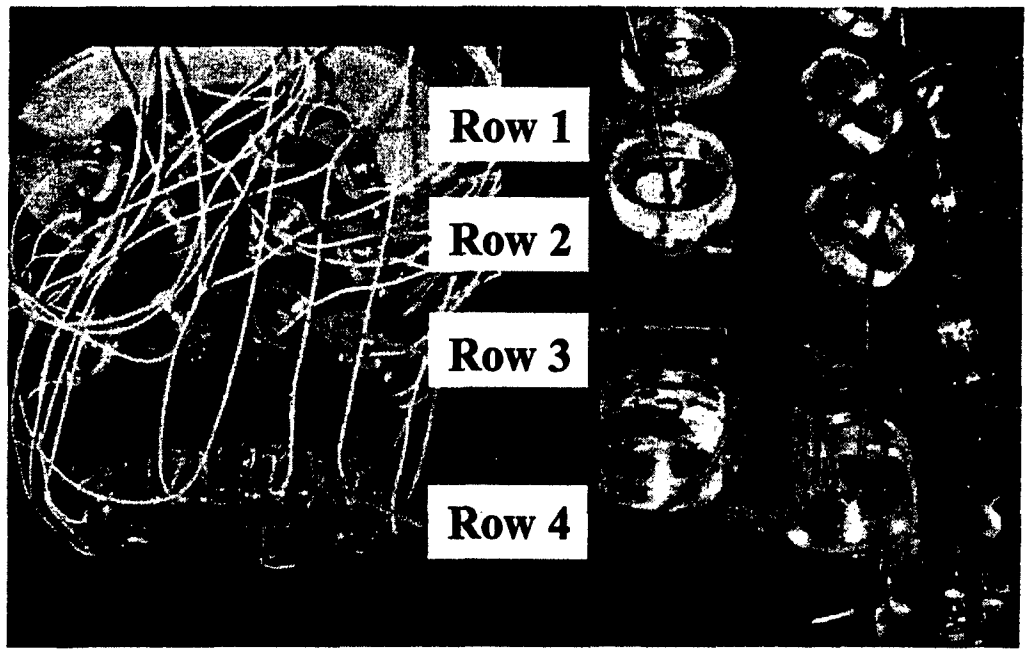


Figure 2. Schematic and picture of electrode holder and individual electrodes orientated both horizontally (bottom) and vertically (sides).

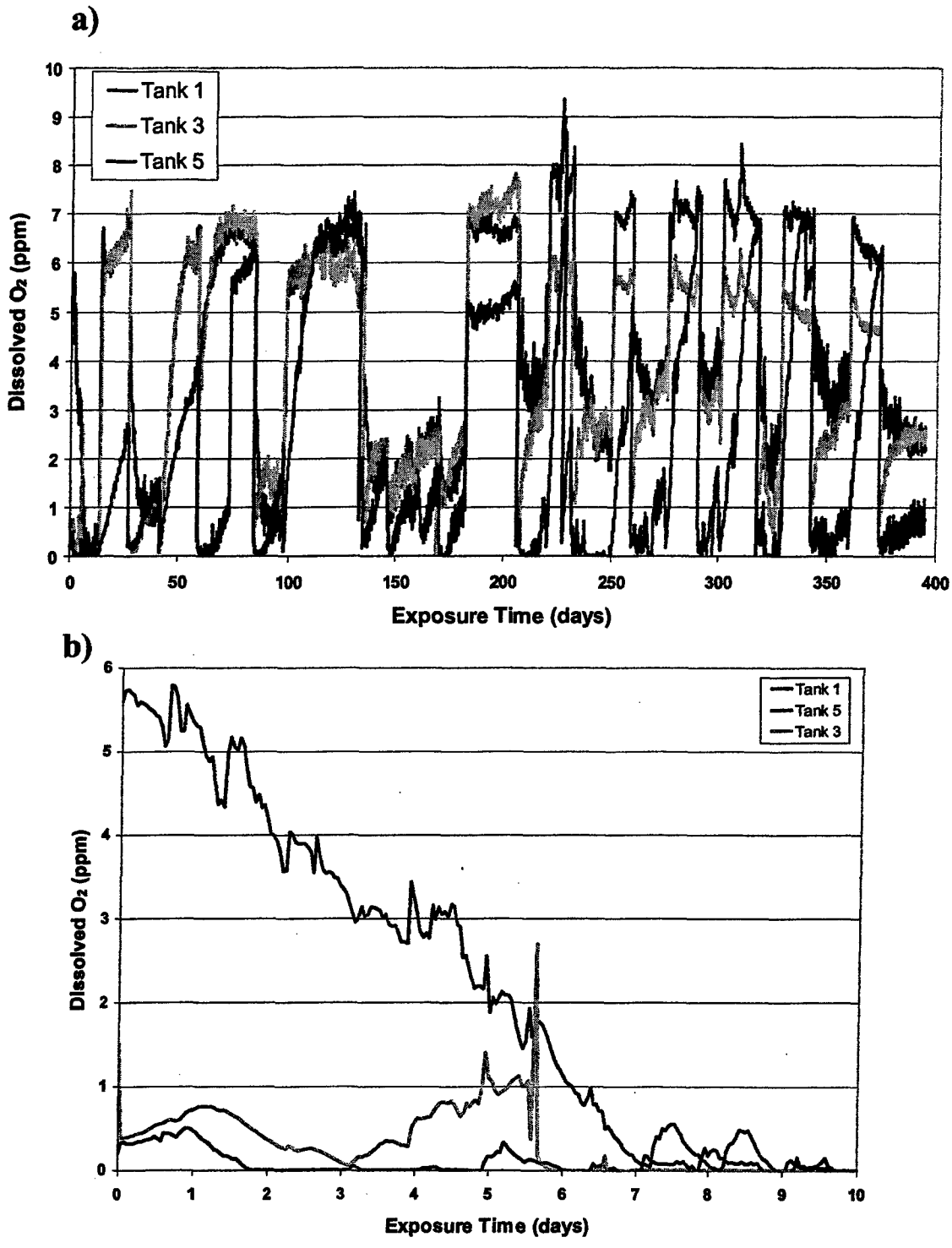


Figure 3. a) Dissolved oxygen (ppm) measured in of Tanks 1, 3 and 5 over the entire 395 day exposure period and b) a close up of the first 10 days of exposure.

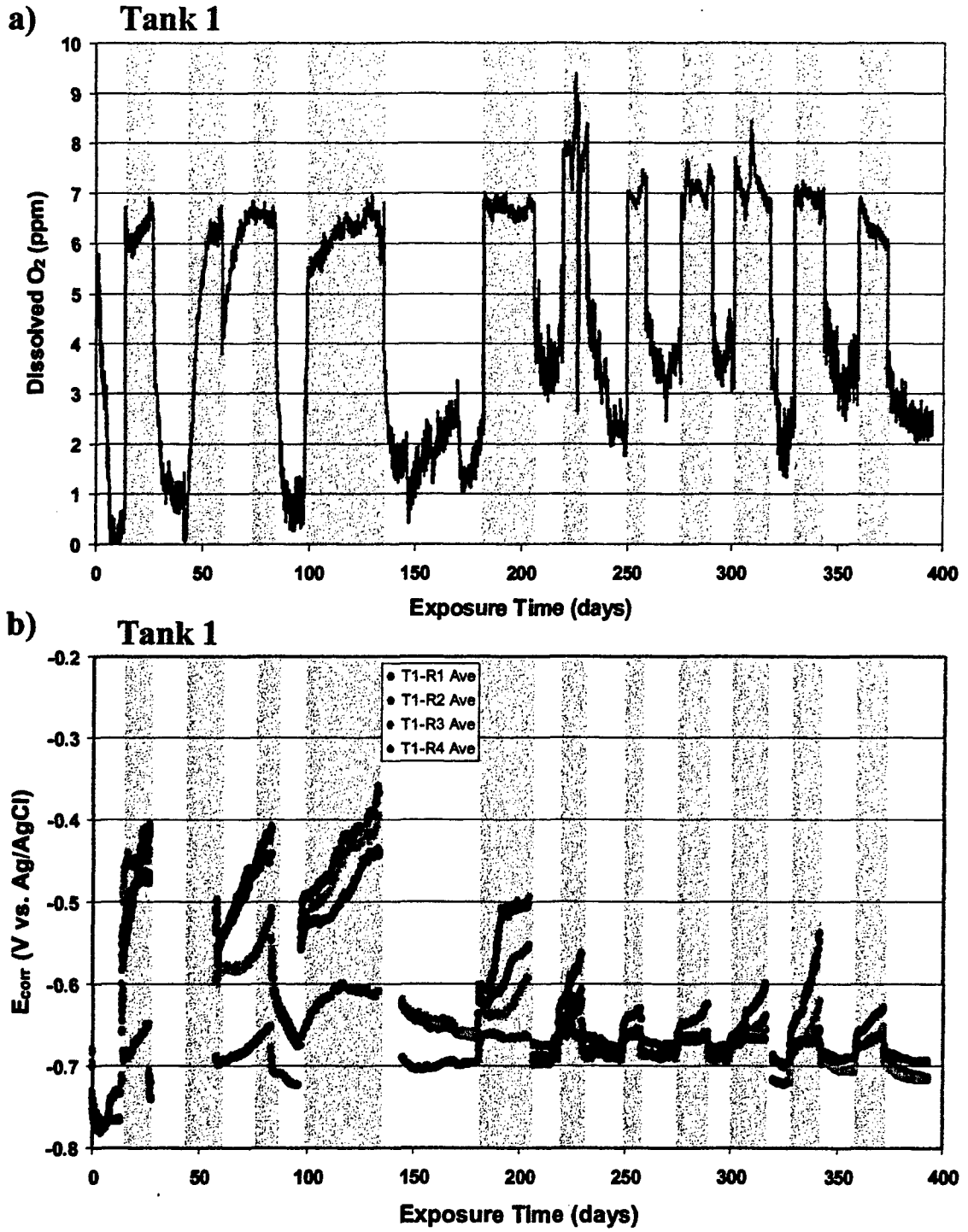


Figure 4. a) Dissolved oxygen levels for Tank 1 with shaded areas indicating empty cycle periods where the seawater was drained and replaced with air. b) Average E_{corr} (vs. Ag/AgCl) values for all four electrode rows exposed in Tank 1.

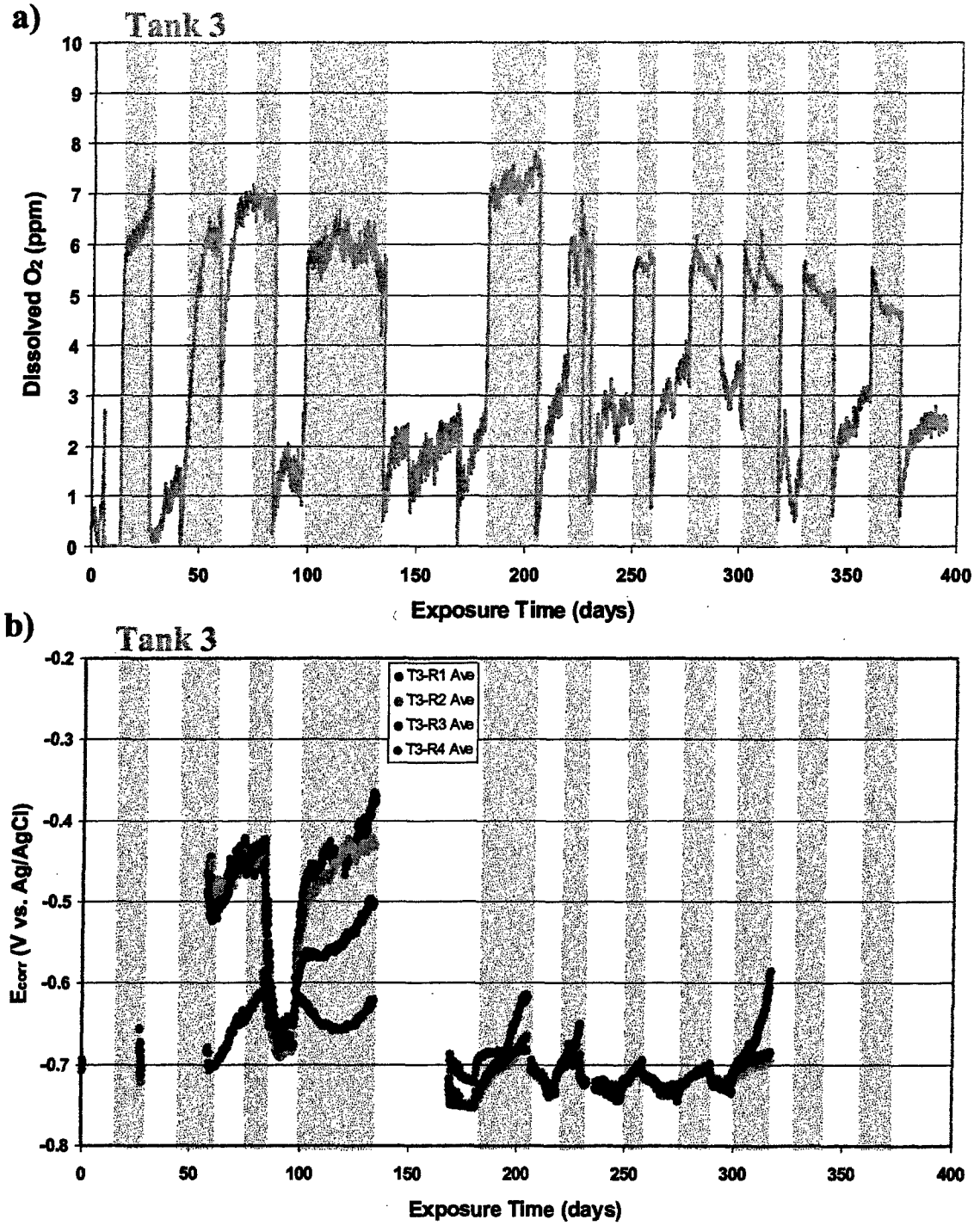


Figure 5. a) Dissolved oxygen levels for Tank 3 with shaded areas indicating empty cycle periods where the seawater was drained and replaced with air. b) Average E_{corr} (vs. Ag/AgCl) values for all four electrode rows exposed in Tank 3.

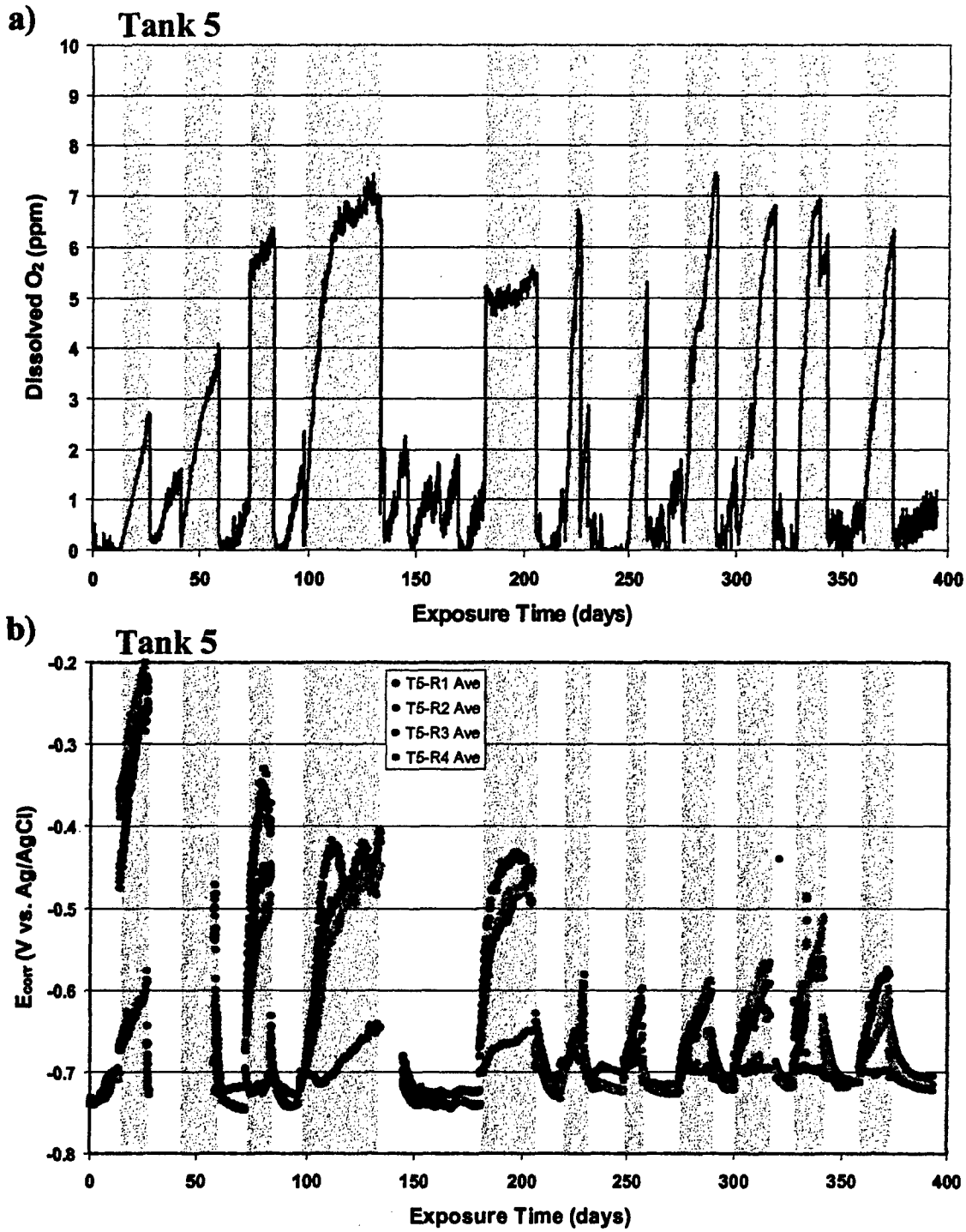


Figure 6. a) Dissolved oxygen levels for Tank 5 with shaded areas indicating empty cycle periods where the seawater was drained and replaced with inert gas. b) Average E_{corr} (vs. Ag/AgCl) values for all four electrode rows exposed in Tank 5.

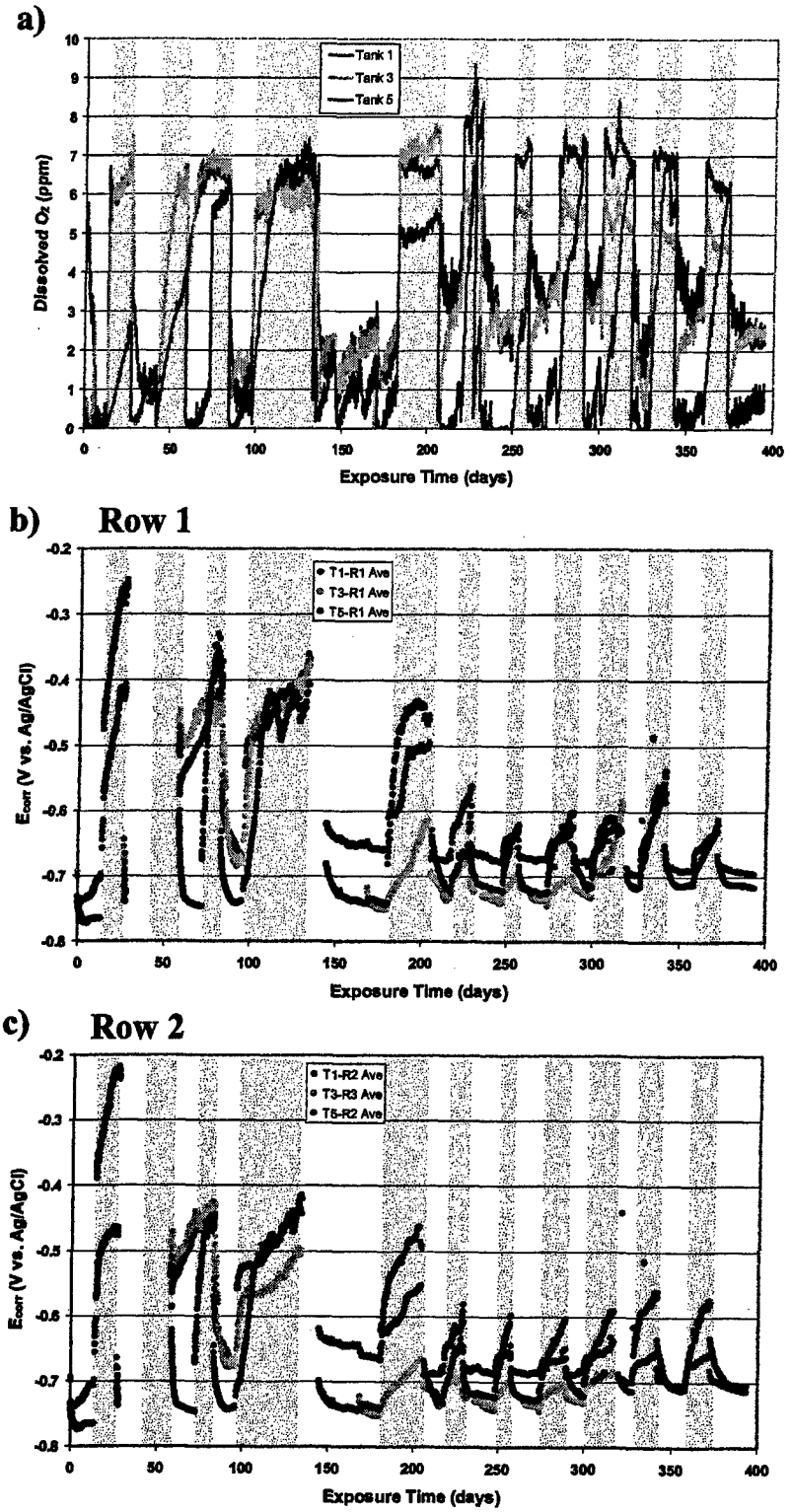


Figure 7. a) Dissolved oxygen (ppm) measured in Tanks 1, 3 and 5 over the 395 day exposure period with shaded areas indicating empty cycle periods where the seawater was drained and replaced with air (Tanks 1 and 3) or inert gas (Tank 5). b) E_{corr} (vs. Ag/AgCl) values for Row 1 electrodes of all three tanks. c) E_{corr} (vs. Ag/AgCl) values for Row 2 electrodes of all three tanks.

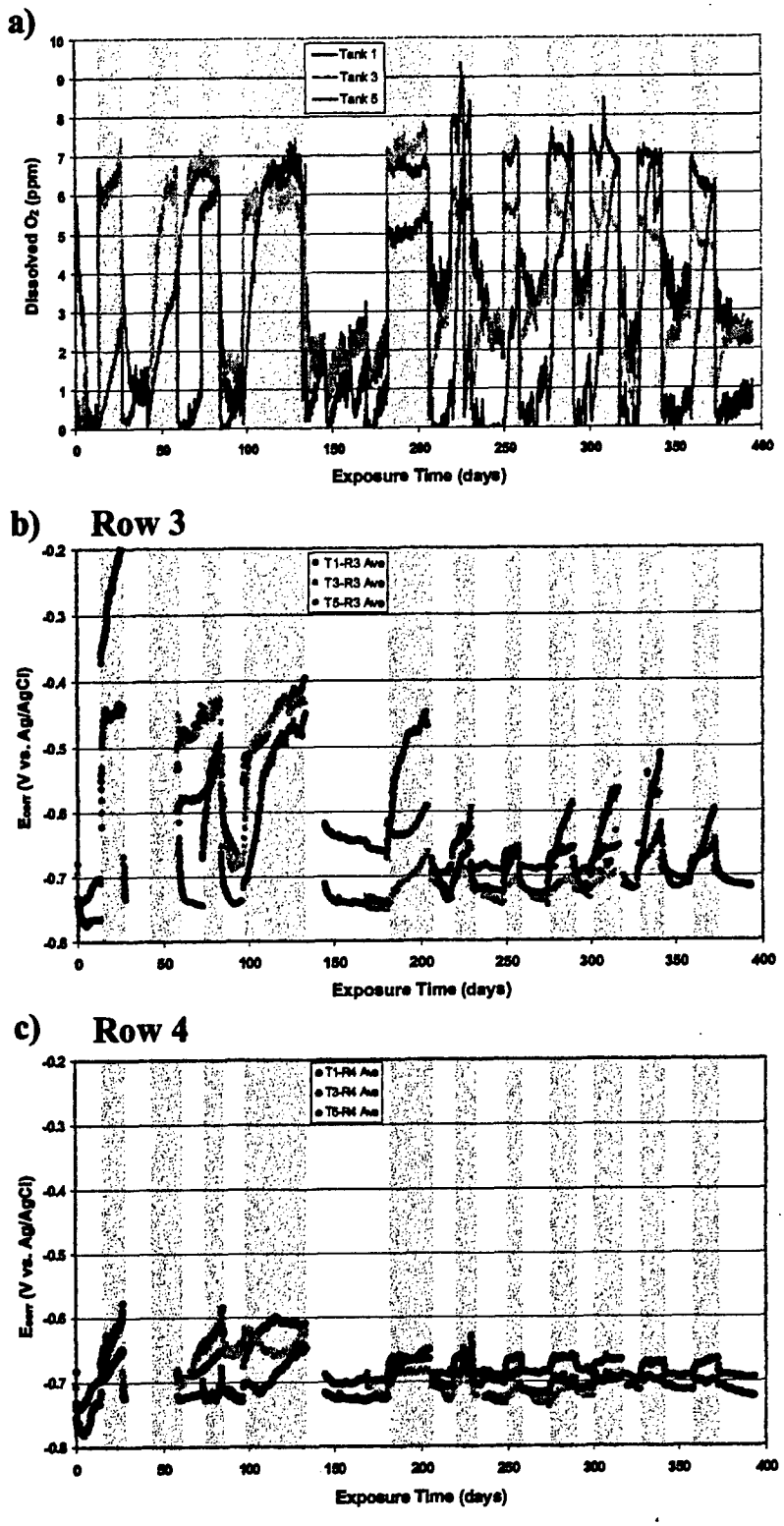
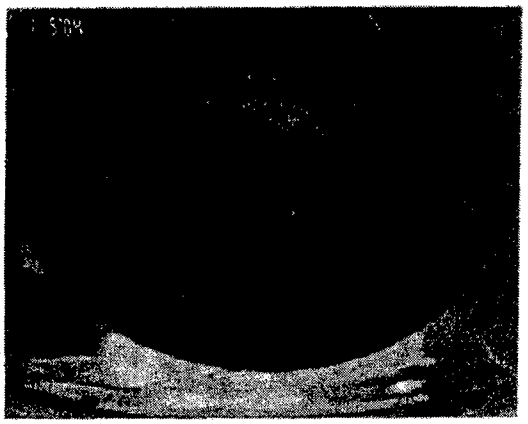


Figure 8. a) Dissolved oxygen (ppm) measured in Tanks 1, 3 and 5 over the 395 day exposure period with shaded areas indicating empty cycle periods where the seawater was drained and replaced with air (Tanks 1 and 3) or inert gas (Tank 5). b) E_{corr} (vs. Ag/AgCl) values for Row 3 electrodes of all three tanks. c) E_{corr} (vs. Ag/AgCl) values for Row 4 electrodes of all three tanks.

a) Tank 5 Row 2 (98 days)

b) Tank 5 Row 2 (146 days)

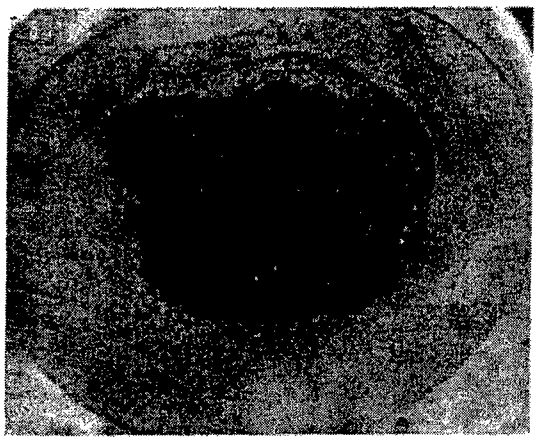
c) Tank 5 Row 2 (237 days)



d) Tank 5 Row 2 (395 days)

Figure 9. Photographs of Row 2 electrodes from Tank 5 after exposure times of 98, 146, 237 and 395 days.

a) Tank 3 Row 1 (395 days)



b) Tank 3 Row 4 (395 days)

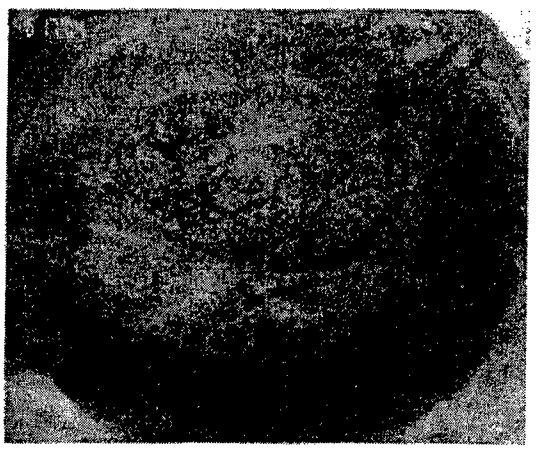


Figure 10. Photographs indicating the different appearance of side (Row 1) and bottom (Row 4) electrodes from Tank 3 after 395 days exposure.

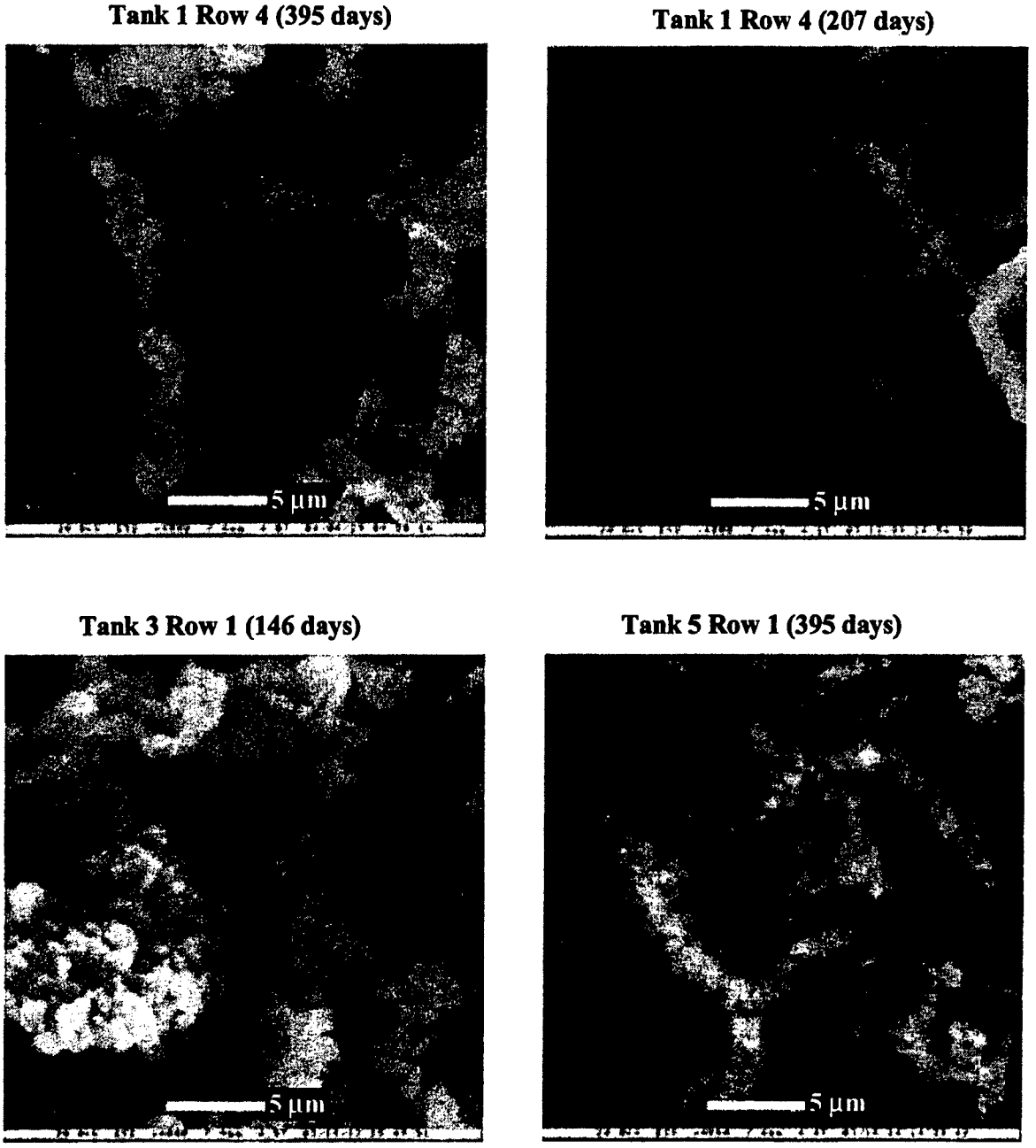


Figure 11. Micrographs of corrosion products from Tanks 1, 3, and 5 from side and bottom rows at various exposure times. Spiral filamentous bacteria can be see with and without encrusted iron corrosion products.

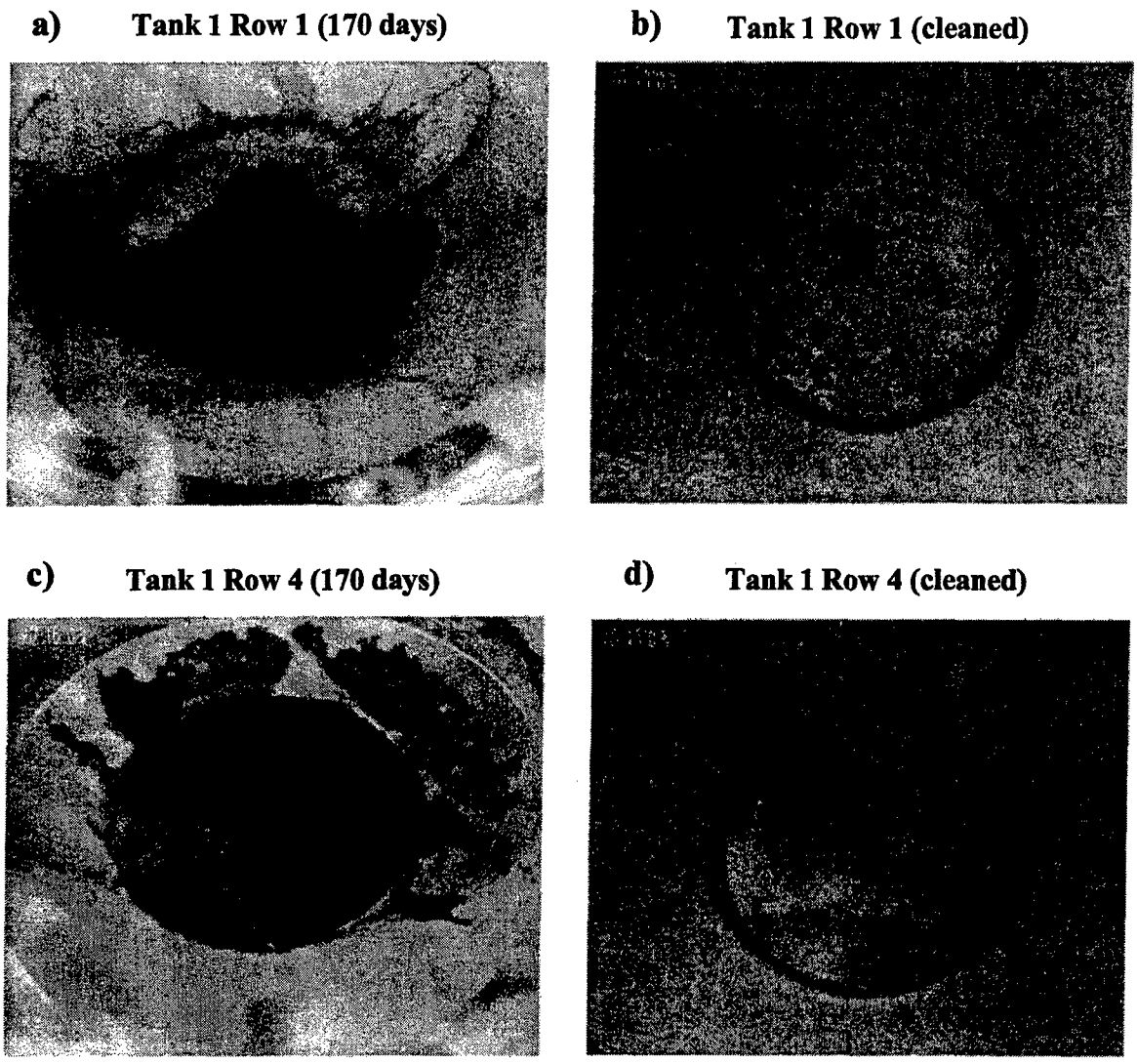


Figure 12. Photographs from Tank 1 electrodes, before and after acid cleaning) from the side (Row 1) and bottom (Row 4) after 170 days exposure. Prior to cleaning, no difference is observed between the two electrodes. However, after cleaning, the Row 1 electrode has evidence of severe localized pitting corrosion while the Row 4 electrode only has evidence of general uniform corrosion.

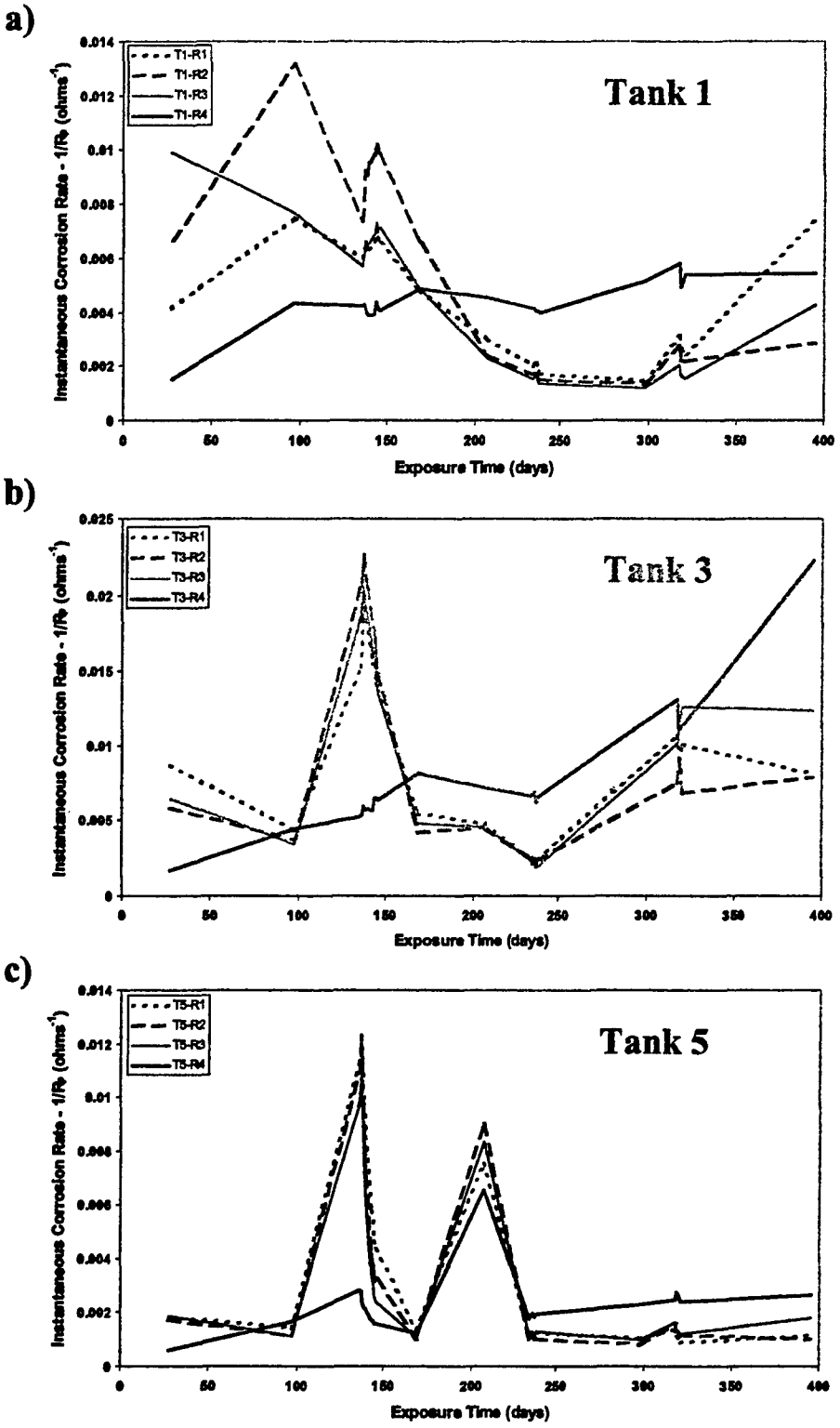


Figure 13. Instantaneous corrosion rates ($1/R_p$ $ohms^{-1}$) of side Rows 1, 2, and 3 and bottom Row 4 electrodes for a) Tank 1, b) Tank 3, and c) Tank 5 over the 395 days exposure.

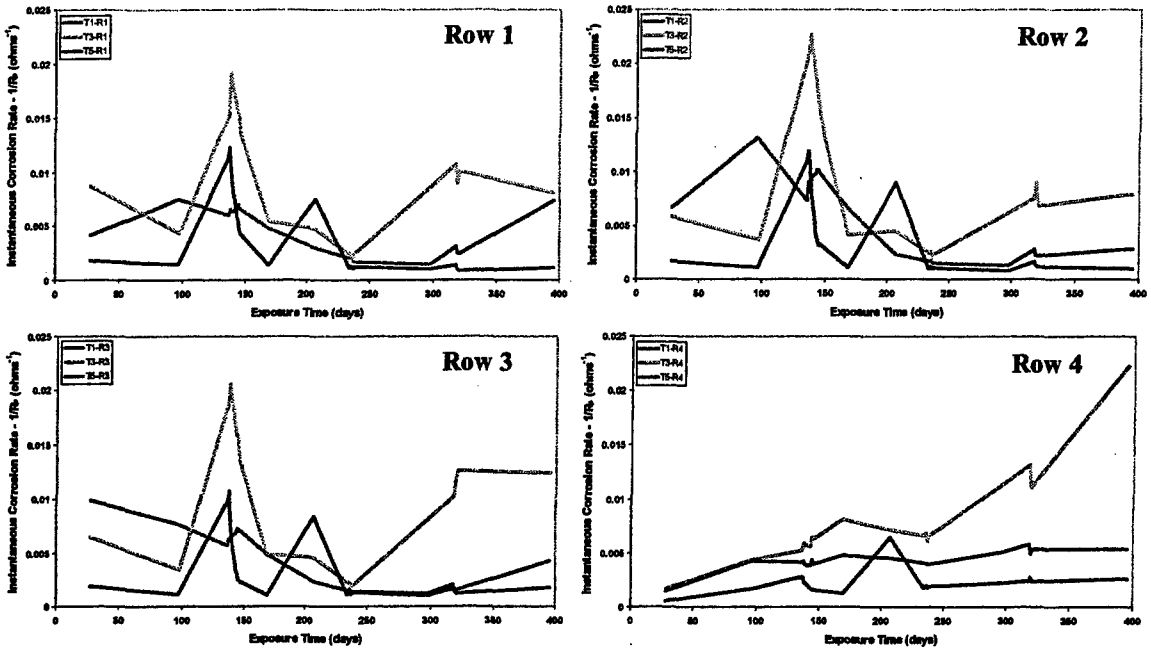


Figure 14. Instantaneous corrosion rates ($1/R_p$ ohms^{-1}) for Tanks 1, 3 and 5 over the 395 days exposure grouped by row.

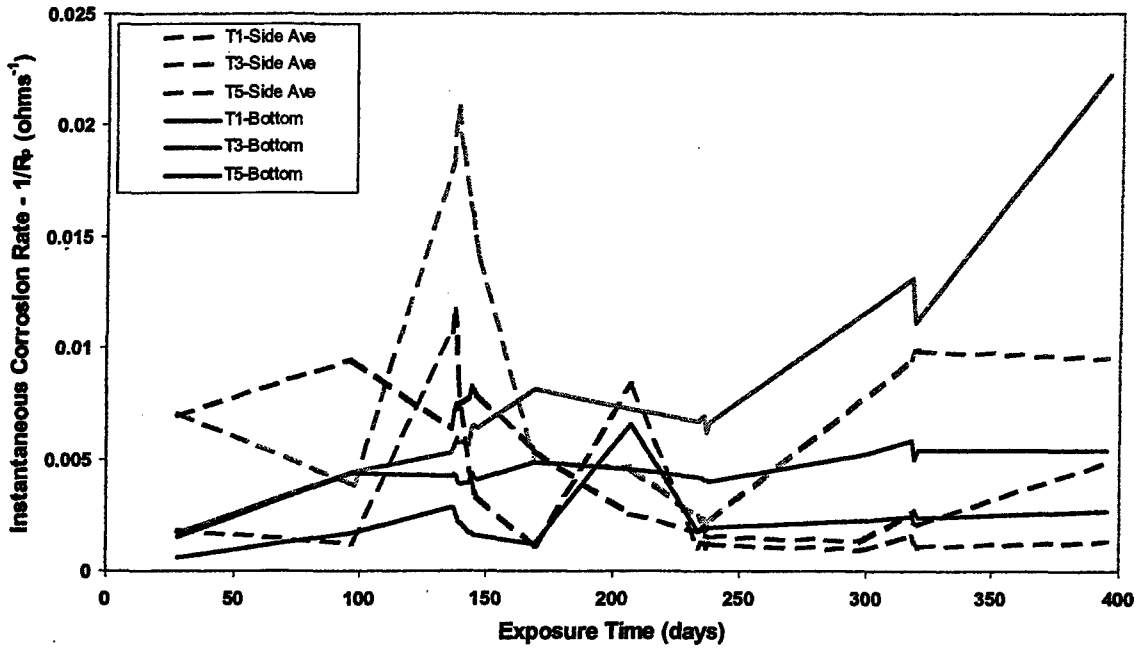


Figure 15. Instantaneous corrosion rates ($1/R_p$ ohms^{-1}) of side (average of Rows 1, 2, and 3) and bottom Row 4 electrodes for Tanks 1, 3, and 5 for 395 days exposure.

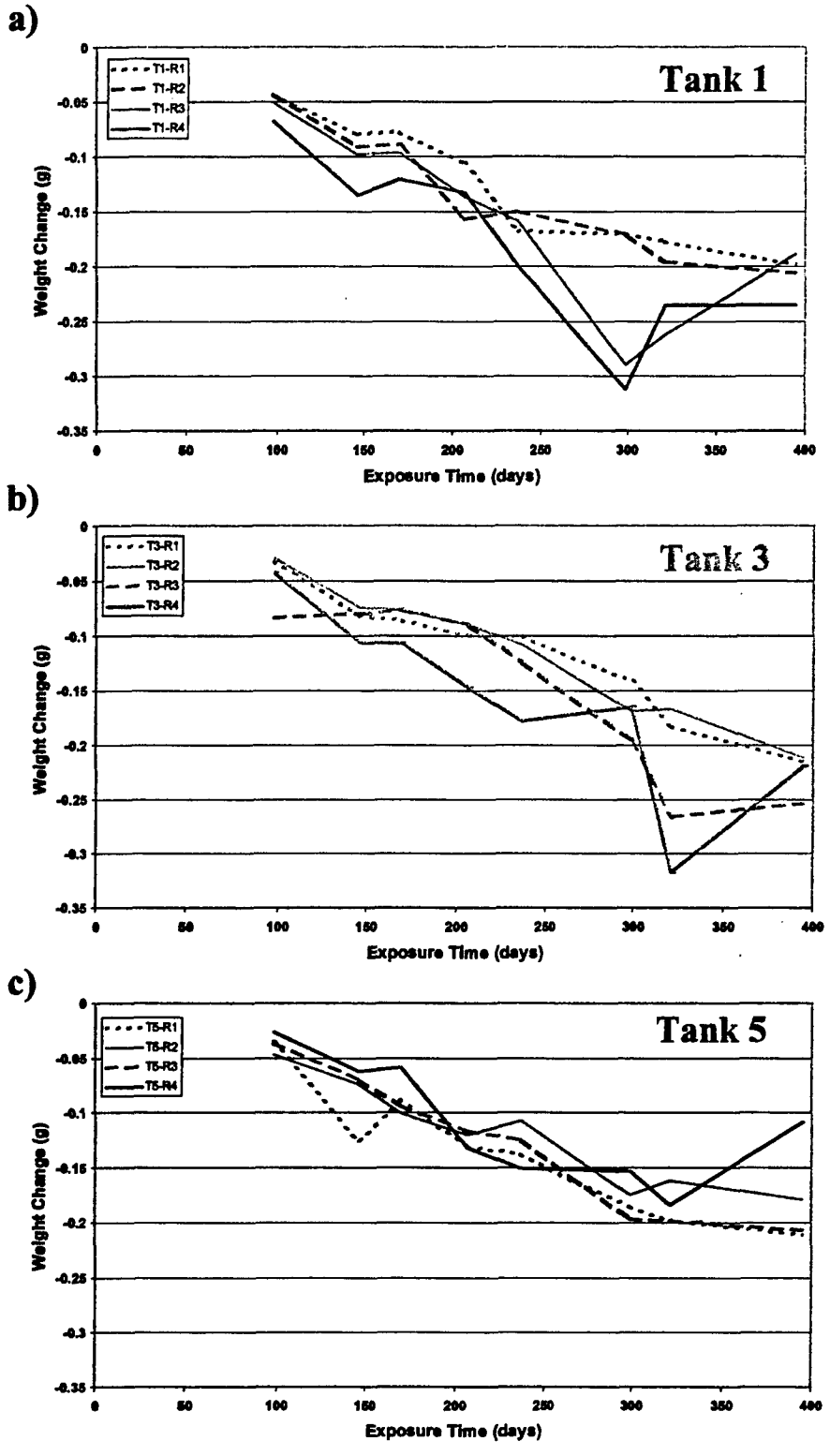


Figure 16. Weight change of electrodes (grams) over the 395 day exposure for a) Tank 1, b) Tank 3 and c) Tank 5.

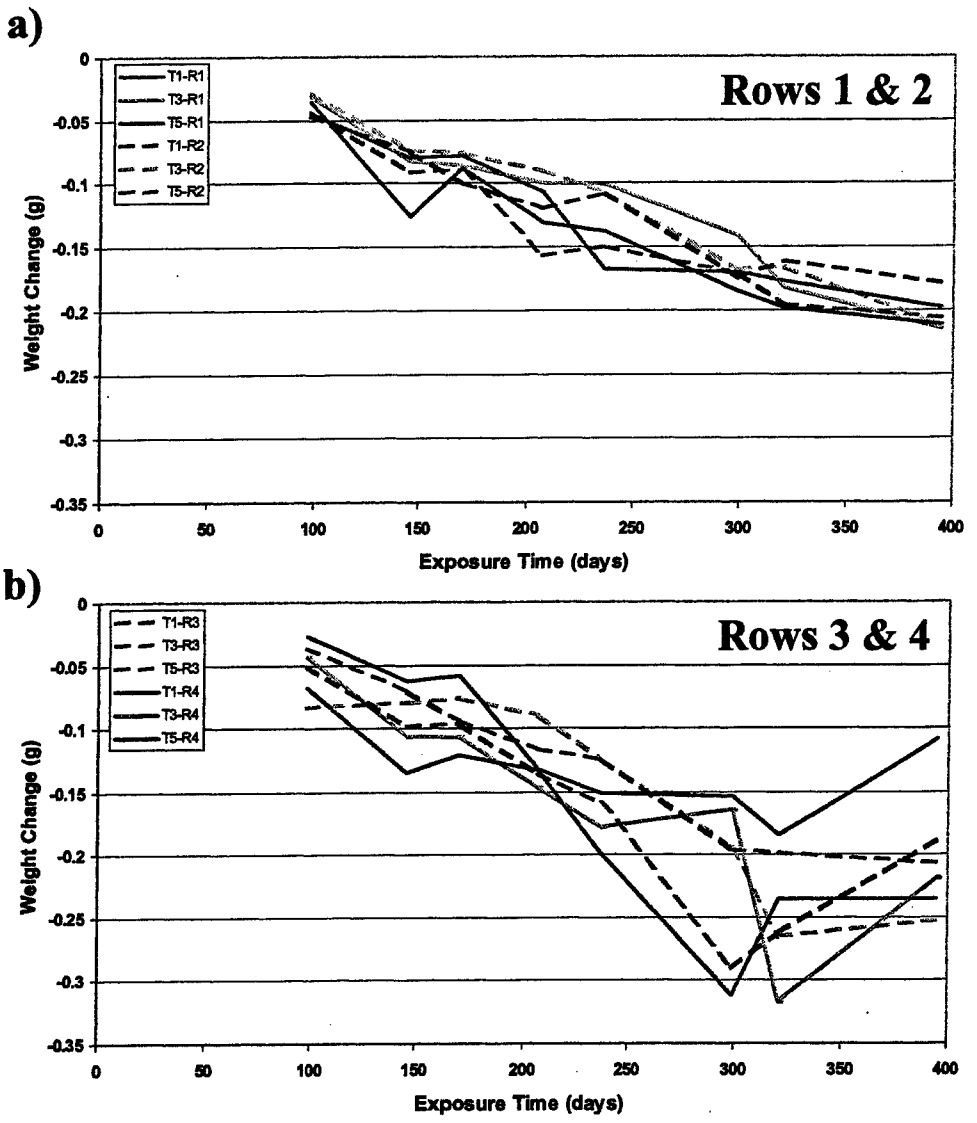


Figure 17. Weight change of electrodes (grams) over the 395 day exposure for Tanks 1, 3 and 5 grouped into a) Rows 1 & 2 and b) Rows 3 & 4.

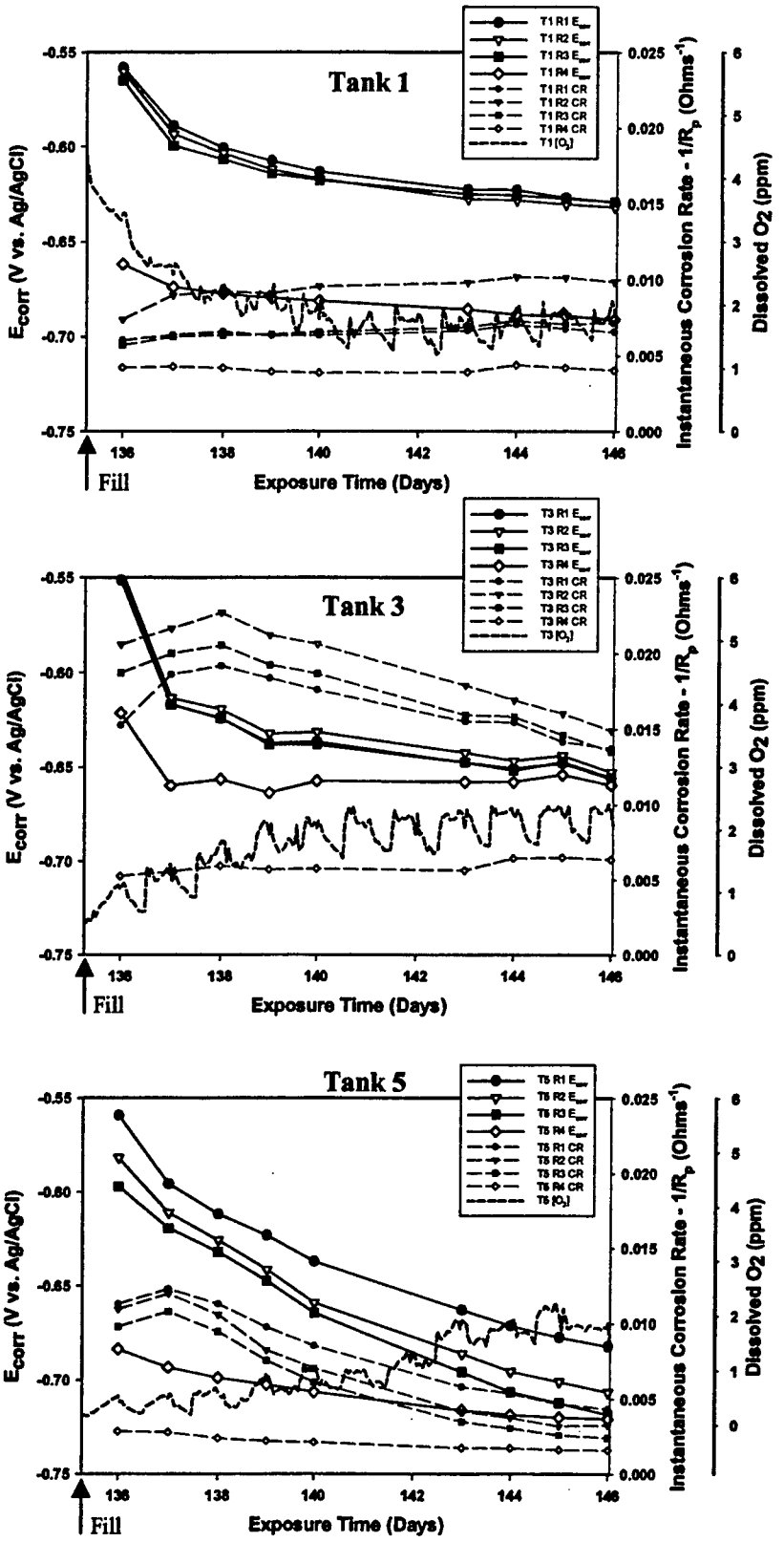


Figure 18. Tank 1 intense data for E_{corr}, dissolved oxygen and $1/R_p$ measurements for the 136 – 146 exposure range of side Rows 1, 2, and 3 and bottom Row 4 electrodes.

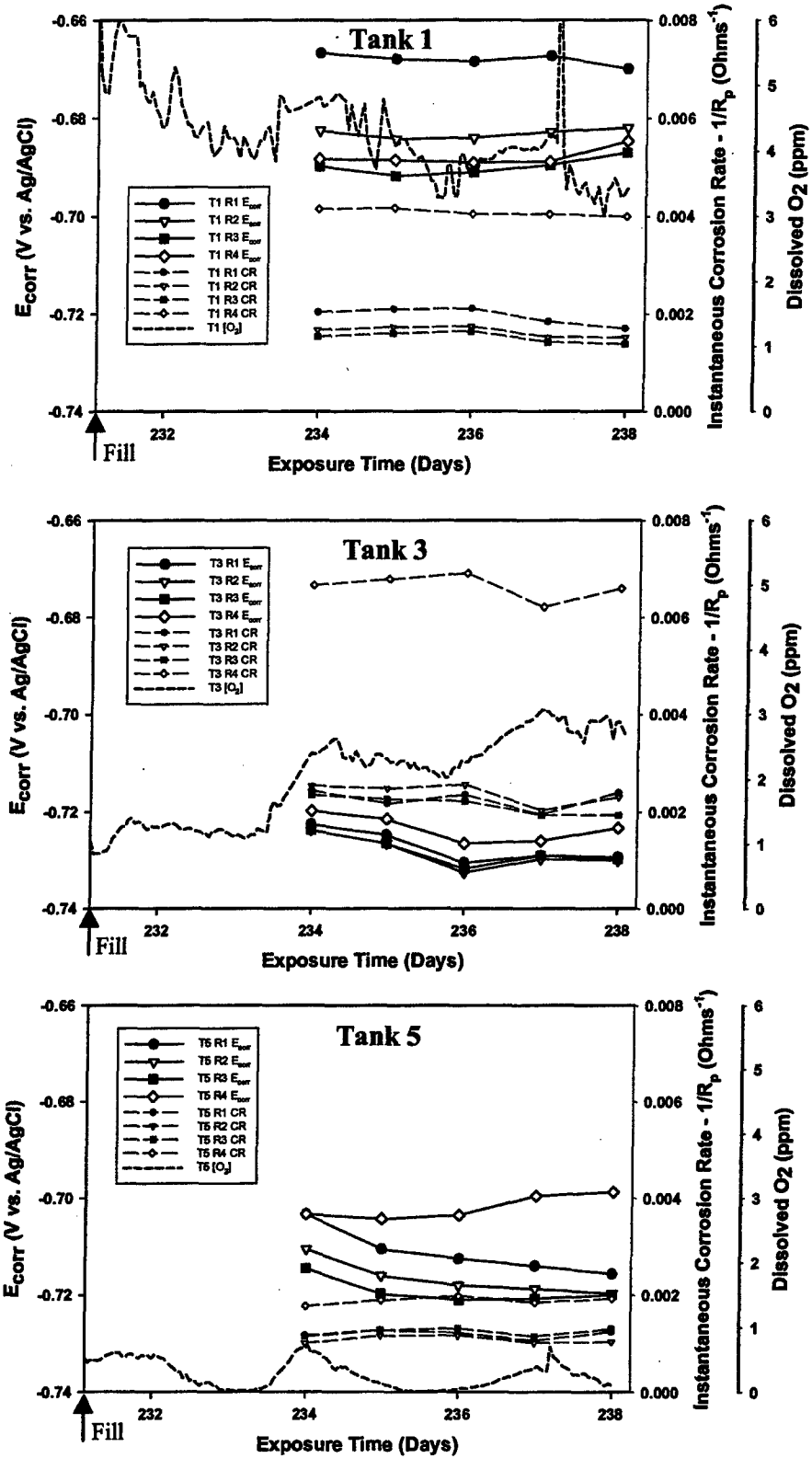


Figure 19. Tank 3 intense data for E_{corr}, dissolved oxygen and $1/R_p$ measurements for the 232 – 238 exposure range of side Rows 1, 2, and 3 and bottom Row 4 electrodes.

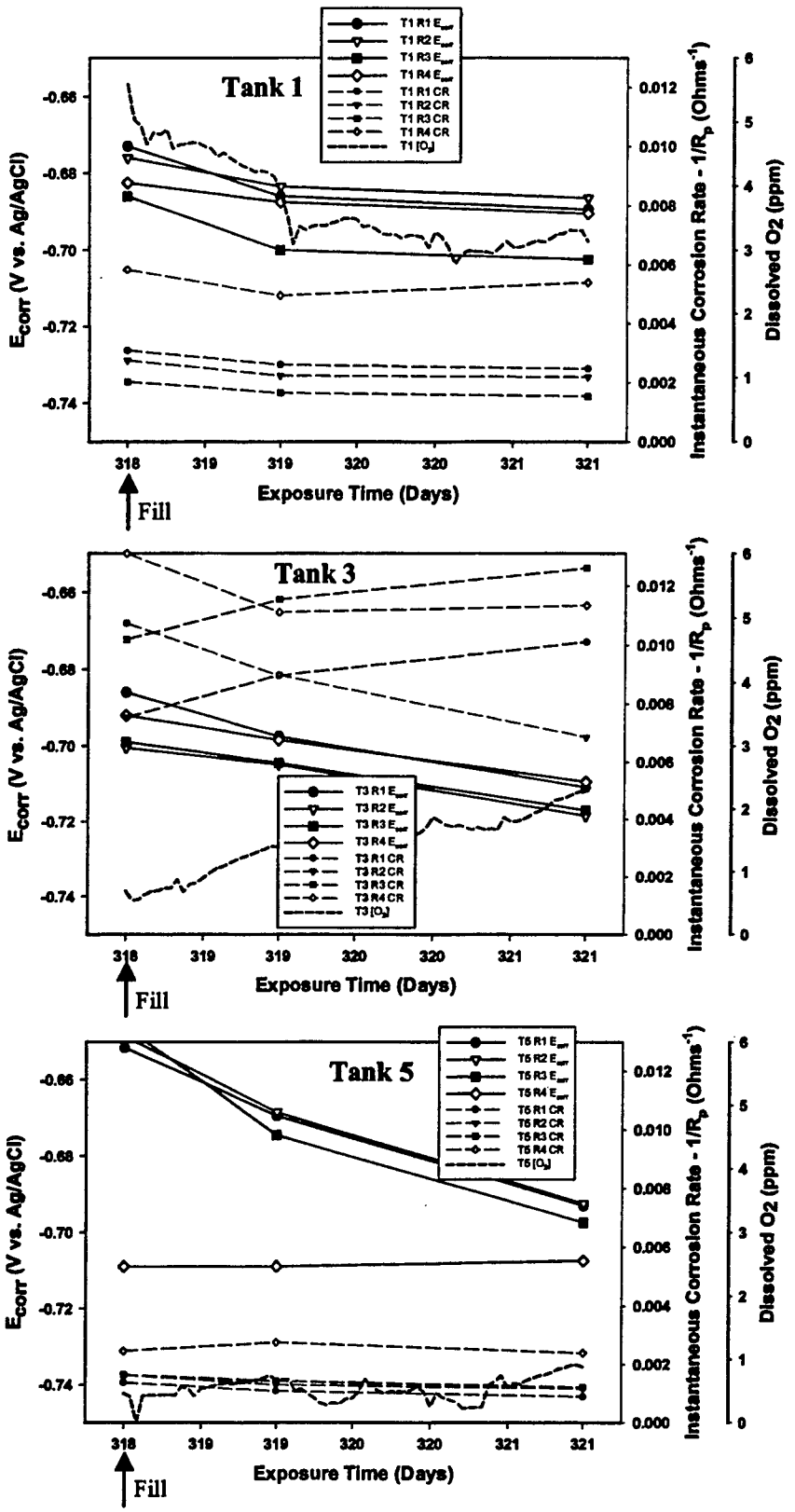


Figure 20. Tank 5 intense data for E_{corr}, dissolved oxygen and $1/R_p$ measurements for the 318 – 321 exposure range of side Rows 1, 2, and 3 and bottom Row 4 electrodes.

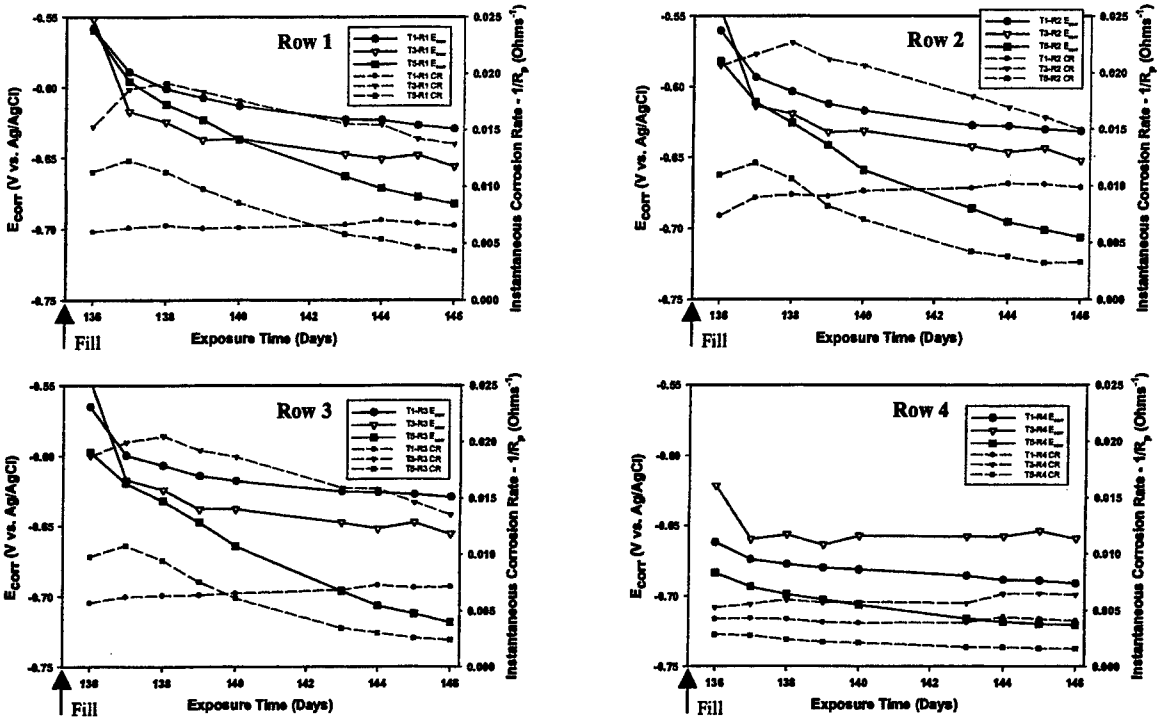


Figure 21. Intense E_{corr} and $1/R_p$ data for the 136 – 146 exposure range for all three tanks and grouped by row.

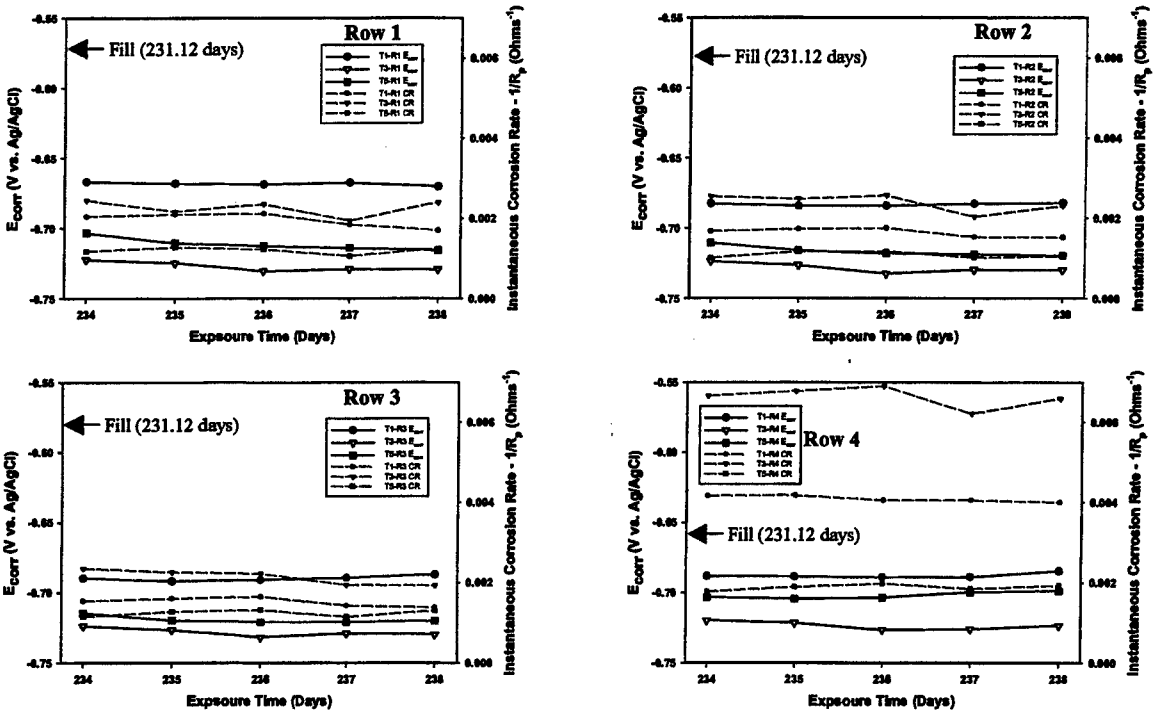


Figure 22. Intense E_{corr} and $1/R_p$ data for the 234 – 238 exposure range for all three tanks and grouped by row.

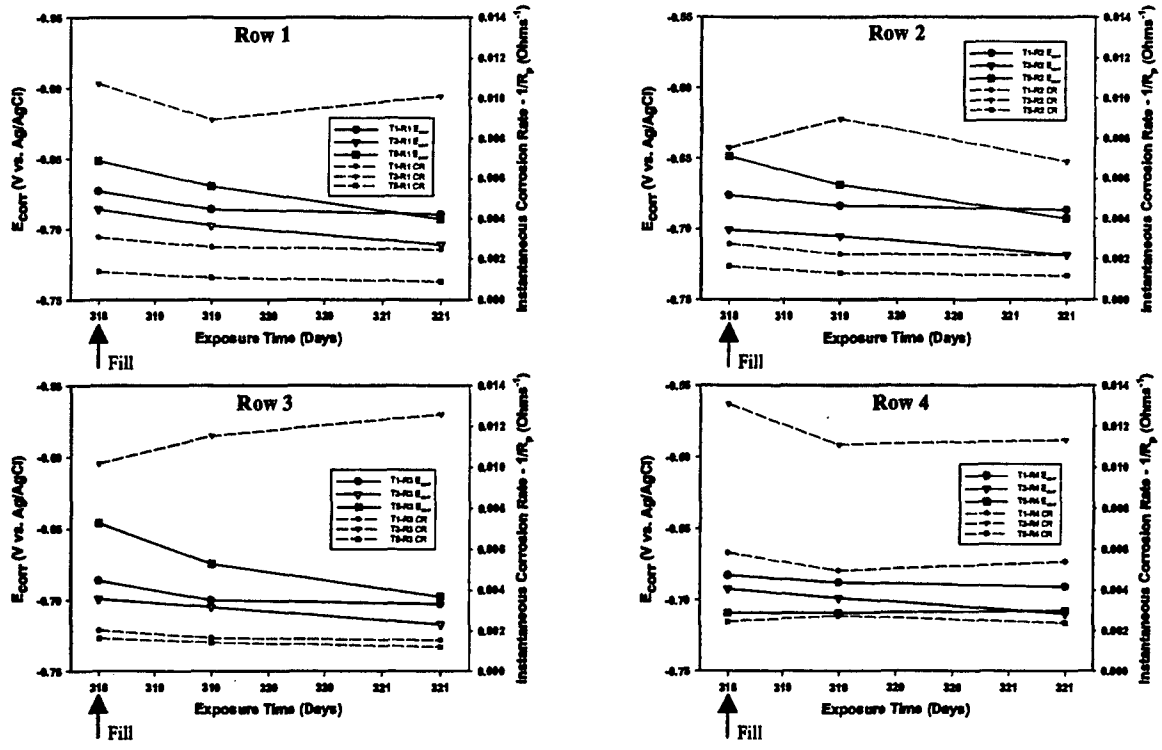


Figure 23. Intense E_{corr} and $1/R_p$ data for the 318 – 321 exposure range for all three tanks and grouped by row.

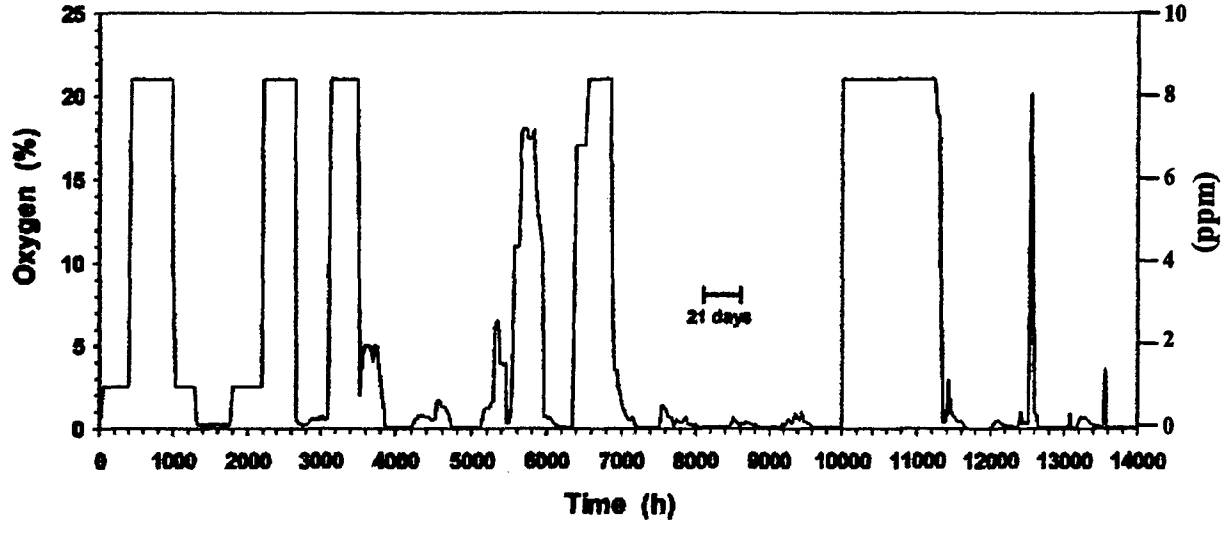


Figure 24. Dissolved oxygen concentration data from Matsuda[2] shipboard experiments of corrosion control using nitrogen to purge ballast tank headspace.

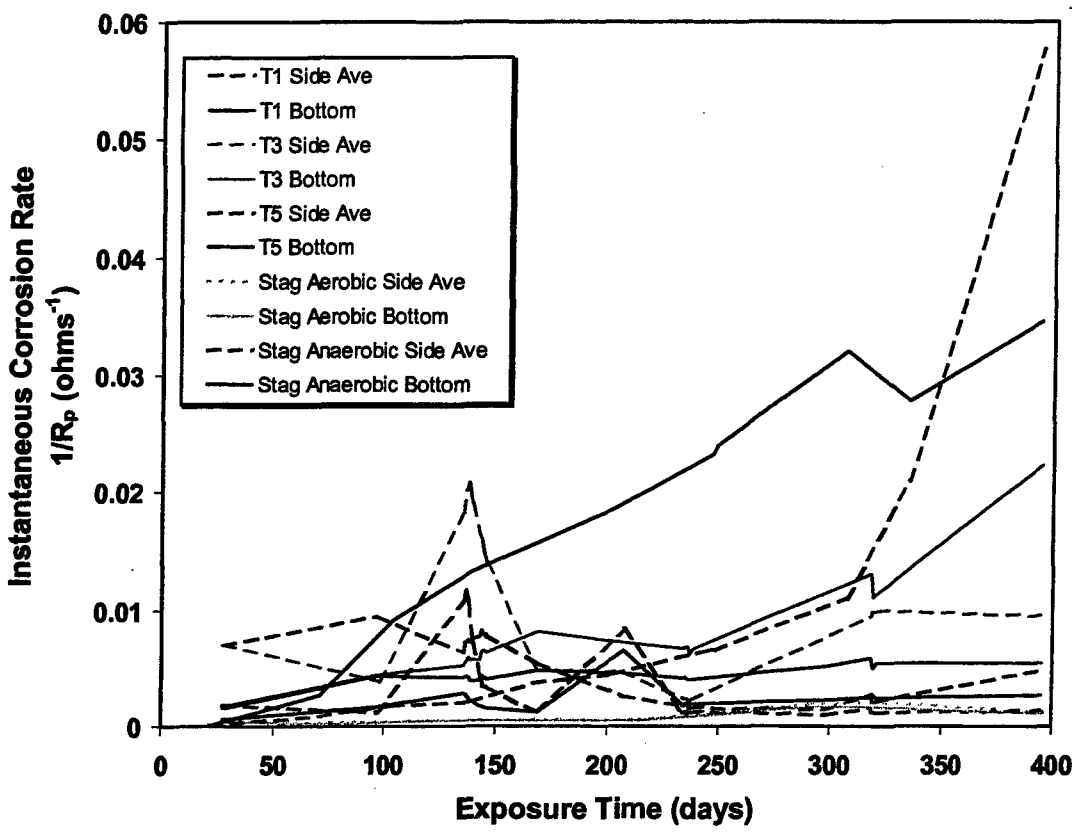


Figure 25. Instantaneous corrosion rates ($1/R_p$ $ohms^{-1}$) of side (average of Rows 1, 2, and 3) and bottom Row 4 electrodes for Tanks 1, 3, and 5 for 395 days exposure (Figure 15) in comparison to stagnant aerobic and stagnant anaerobic conditions. Stagnant aerobic conditions had the lowest corrosion rates while the bottom row of the stagnant anaerobic case had the largest.